

A066307

LEVEL III

R/W

11
12

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

7064308

VOLUME I EXPLOSIVES RELATED CHEMICALS

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

DDC
RECEIVED
APR 6 1979
RECEIVED

A

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an
official Department of the Army position unless so design-
ated by other authorized documents.

79 04 13

DDC FILE COPY

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
5. TITLE (and Subtitle) Preliminary Problem Definition Study of 48 Munitions Related Chemicals. Volume I - Explosives Related Chemicals.		6. TYPE OF REPORT & PERIOD COVERED Final Report. October 1977-April 1978.
7. AUTHOR(s) J. F./Kitchens, W. E./Harward III, D. M./Lauter, R. S./Wentzel, R. S./Valentino		8. PERFORMING ORG. REPORT NUMBER 49-5730-01
9. PERFORMING ORGANIZATION NAME AND ADDRESS Atlantic Research Corporation 5390 Cherokee Avenue Alexandria, Virginia 22314		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62620A 3E762720 AB35.00.003
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Medical Research and Development Command Ft. Detrick, Frederick, Maryland 21701		12. REPORT DATE April 1978
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (D) 272p.1		13. NUMBER OF PAGES 302
		15. SECURITY CLASS. (of this report) Unclassified
		18a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release Distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Explosives dimethylamine 1,3 dinitrobenzene pollution cyclohexanone trimethylamine 1,3,5-trinitrobenzene hazards hexamine TAX uses toxicology methylamine SEX production		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Results are presented of a preliminary problem definition study on propellant related chemicals. The purpose of this study was to determine the Army's responsibility for conducting further research on these chemicals to determine toxicological and environmental hazards, so that effluent stan- dards can be recommended. Both civilian and military uses of the chemical were evaluated.		

70 03.22 -1-

045 550

LB

PRELIMINARY PROBLEM DEFINITION STUDY OF 48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

ATTENTION TO	
DTIC	DTIC ACTION <input checked="" type="checkbox"/>
DDP	DDP ACTION <input type="checkbox"/>
UNCLASSIFIED	<input type="checkbox"/>
JUSTIFICATION	<input type="checkbox"/>
BY	
DISTRIBUTION/AVAILABILITY CODES	
NO.	AVAIL. AND/OR SPECIAL
A	

DDC
RECEIVED
APR 6 1979
A

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

"Permission for the publication herein by Sadtler Standard Spectra® has been granted, and all rights are reserved, by Sadtler Research Laboratories, Inc."

SUMMARY

The goal of this preliminary problem definition study was to assess the Army's responsibility for further study on forty-eight (48) chemicals associated with munitions production. This report covers the study results on the nine chemicals used or produced in manufacture of explosives:

- | | |
|------------------|-------------------------|
| - hexamine | - SEX |
| - cyclohexanone | - TAX |
| - methylamine | - 1,3-dinitrobenzene |
| - dimethylamine | - 1,3,5-trinitrobenzene |
| - trimethylamine | |

The recommendations resulting from the study are summarized in Table S-1 and discussed below:

Hexamine

Hexamine is one of the starting materials used in the manufacture of RDX and HMX at Holston AAP. In 1975, Holston AAP purchase of hexamine was 32% of the civilian production. At full mobilization, the Army's purchase of hexamine would be 75% of the civilian production capacity.

The major civilian usage of hexamine is as a methylenating agent for crosslinking in thermosetting phenolic resins. It is also used as an intermediate in the production of nitrilotriacetic acid, an accelerator in the rubber industry and an urinary antiseptic.

Hexamine itself is relatively non-toxic to mammalian and aquatic life. However, under acidic conditions or microbial attack, hexamine decomposes to formaldehyde and ammonia. These compounds are toxic to aquatic organisms.

The major discharge of hexamine at Holston AAP is from the Building A-1 still. This still currently operates only one week out of every four months. At full mobilization, the still would operate on a continuous basis. When this still is in operation, high concentrations of hexamine are discharged into the Arnott Branch. The hexamine discharge could result in high levels of formaldehyde and ammonia in the Branch.

The Army's further effort on hexamine should be concentrated on an effective treatment process for removal of hexamine from the Holston waste streams. Further literature evaluation of the toxicological and environmental hazards of hexamine should be a low priority.

Cyclohexanone

Cyclohexanone is used as a recrystallization solvent in the manufacture of RDX at Holston Army Ammunition Plant (HAAP). At current production levels, Holston AAP utilizes 180,000 lb of cyclohexanone per year. This solvent is purchased from civilian manufacturers. At full mobilization, 2 million lb per year of cyclohexanone would be used.

ACCESSION	
RTIS	While Section <input checked="" type="checkbox"/>
CDS	Buff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODE	
Dist.	AVAIL. and/or SPECIAL
A	

Table S-1. Summary of Recommendations for Future Work in Explosives Related Chemicals.

	Phase II Studies		Other Recommended Studies
	Toxicological	Environmental	
Hexamine	no	no	Investigation of treatability of A-1 still sludge.
Cyclohexanone	no	no	Further identification and quantification of cyclohexanone addition compounds in HAAP wastes. Phase II type of study on cyclohexanone addition compounds.
Methylamine	no	yes	Effluent stream analysis at HAAP.
Dimethylamine	no	yes	Effluent stream analysis at HAAP.
Trimethylamine	no	yes	Effluent stream analysis at HAAP.
SEX	yes	yes	Effluent stream analysis at Holston. Possibly toxicology study.
TAX	yes	yes	Effluent stream analysis at Holston. Possibly toxicology study.
1,3-dinitrobenzene	yes	yes	Sediment accumulation & bioaccumulation studies. Fate of these compounds in the proposed biotreatment facilities.
1,3,5-trinitrobenzene	yes	yes	Sediment accumulation & bioaccumulation studies. Fate of these compounds in the proposed biotreatment facilities.

The civilian cyclohexanone production capacity is 1590 million lb/year. The major civilian uses of cyclohexanone is as a chemical intermediate in the manufacture of nylon 66 and nylon-6. It is also used in the manufacture of caprolactone and as a solvent.

The Army's use of cyclohexanone at full mobilization is only 0.38% of the 1975 United States production. At full mobilization, the Army's discharge of cyclohexanone would represent only 4% of the 1974 civilian air emissions of this compound. Thus, cyclohexanone is not a military unique compound.

Cyclohexanone is moderately toxic to mammals. Sublethal doses cause profound narcosis accompanied by central nervous system depression. The aquatic toxicity of cyclohexanone is low.

In the environment, cyclohexanone is degraded by photochemical and microbial pathways. In the presence of formaldehyde, addition products are formed. Quantitative information on the formation of these products in the effluents streams is not available.

Further studies by the Army on the toxicological and environmental properties of cyclohexanone should be a low priority. However, the formation of cyclohexanone addition compounds in the effluent streams at Holston AAP should be further investigated. This investigation should include identification and quantification of these compounds and a literature evaluation of their toxicological and environmental hazards.

Methylamine

The methylamines are by-products of the RDX/HMX manufacture at Holston AAP. The only documented entrance of these compounds into the environment is from the A-1 still sludges. When operating, this still discharges 613 lb/day of methylamine, 385 lb/day of dimethylamine and 31.5 lb/day of trimethylamine into Arnett Branch. The presence of high concentrations of nitrate lead to the possibility of formation of the potent carcinogen, N-nitrosodimethylamine, in this waste stream.

The methylamines are produced in large quantities by the civilian community. Current production capacity is ~323 million lb/year of mono-, di- and trimethylamine in the equilibrium ratio. The methylamines are used as synthetic intermediates for synthesis of choline chloride, dimethylformamide, dimethylacetamide, insecticides and surfactants.

The methylamines are widespread through the ecosystem. They are not toxic in small amounts to mammals, fish, microorganisms and plants. Microbial degradation occurs in the environment. However, in the presence of nitrate or nitrite, dimethyl- and trimethylamine can be biologically converted to N-nitrosodimethylamine.

The methylamines are not military unique compounds. Their toxicological properties have been studied in detail. Further toxicological work by the Army should be a low priority. Holston has a unique situation of high nitrate and high dimethylamine content in its wastes. Thus, there exists the potential formation of N-nitrosodimethylamine. Therefore, environmental fate of the methylamines should be further investigated. Effluent stream analysis at Holston AAP should complement this study.

SEX and TAX

SEX and TAX are acetylated nitramines by-products formed during the manufacture of RDX/HMX at Holston AAP. These military unique compounds enter the environment from the acid wash and dewatering operations. The levels of SEX in these waste streams are 20-40% of the RDX concentrations. TAX levels are between 60-90% of the RDX concentrations.

The toxicity and environmental fate of these chemicals have not been extensively studied. However, contacts with foreign manufacturers and comparison to similar compounds could yield useful information on the toxicological and environmental hazards of these compounds. It is, therefore, recommended that a Phase II effort on these compounds be initiated. In addition, further effluent stream analysis at Holston AAP is needed. Acute mammalian and aquatic toxicity and *in vivo* mutagenic studies may be warranted depending on the results of the Phase II study.

1,3-dinitrobenzene

1,3-dinitrobenzene is a by-product of the manufacture of TNT at Radford, Volunteer, Joliet and Newport Army Ammunition Plants. This compound is formed by nitration of the benzene impurities present in the toluene starting material. Most of the 1,3-dinitrobenzene formed in the process is not removed from the TNT and is thus an impurity in the final product. However, a small amount of this compound (0.2 to 2 lb line/day) is discharged in the red water evaporation condensate.

Since 1,3-dinitrobenzene is found in the TNT final product, it can also enter the environment from TNT blending at Holston Army Ammunition Plant and the LAP plants. 1,3-dinitrobenzene can also be produced in the environment by photolysis of 2,4-dinitrotoluene. Once formed, 1,3-dinitrobenzene does not undergo further photochemical decomposition.

There is one civilian manufacturer of 1,3-dinitrobenzene in the United States. All the product produced in the civilian sector is used as a synthetic intermediate, mainly in the dye industry. The pollution from 1,3-dinitrobenzene from the civilian manufacture and use is not known. However, it is probably far less than that from TNT production and use at full mobilization.

1,3-dinitrobenzene is highly toxic to mammalian and aquatic life. It is slowly degraded by microorganisms. However, under most environmental

conditions, this degradation is small and 1,3-dinitrobenzene accumulates in sediments.

In view of the toxicity and the apparent widespread Army pollution, it is recommended that 1,3-dinitrobenzene be included in the Phase II study. It is also recommended that additional experimental studies be conducted to clarify the environmental fate of 1,3-dinitrobenzene and the effectiveness of planned treatment processes for removing this compound from the effluent streams.

1,3,5-trinitrobenzene

1,3,5-trinitrobenzene is an explosive formed in small amounts during the manufacture of TNT at Radford, Volunteer, Joliet and Newport Army Ammunition Plants. This compound is formed by competitive oxidation of TNT to 2,4,6-trinitrobenzoic acid followed by decarboxylation.

Most of the trinitrobenzene formed is found in the final TNT product. However, small amounts are discharged in the evaporator condensate from the evaporation of red water. Estimates of the 1,3,5-trinitrobenzene discharges from the manufacture of TNT are 0.39 lb/line/day.

Since 1,3,5-trinitrobenzene is formed in concentrations of 0.1 to 0.7% of the TNT product, it can also be found in effluent from blending operations at Holston AAP and loading (LAP) at Joliet AAP, Cornhusker, Kansas, Lone Star, Louisiana and Iowa AAPs. Estimated discharges from blending operations at Holston could be as much as 9 lb/day. The discharges from the LAP facilities vary depending on how the pink water is handled. Cornhusker, Kansas, Lone Star and Louisiana dispose of pink water in evaporation ponds. Joliet and Iowa have carbon adsorption columns.

In addition to the 1,3,5-trinitrobenzene in the effluent from the manufacture, blending and loading of TNT, 1,3,5-trinitrobenzene is formed photochemically from TNT in the waste water. It is estimated that 1% of the TNT discharged is converted to 1,3,5-trinitrobenzene. This compound is not further photochemically degraded.

1,3,5-trinitrobenzene is toxic to both mammalian and aquatic life. It does not appear to degrade significantly in the environment and thus accumulates in sediments.

1,3,5-trinitrobenzene is a unique military chemical. Some minor pollution may occur from civilian manufacture of nitrated aromatics. However, the military pollution arising from this compound in the process effluents and from photodecomposition of TNT in the environment is the major source of 1,3,5-trinitrobenzene in the environment.

The following recommendations are made for 1,3,5-trinitrobenzene:

- Phase II study be initiated
- additional sampling at RAAP or VAAP (when operational) and HAAP be carried out to determine the extent of sediment and biological accumulation.

FOREWORD

This report details the results of a preliminary problem definition study on explosives related chemicals. The purpose of this study was to determine the Army's responsibility for conducting further research on these chemicals in order to determine their toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on these explosives related chemicals, the military and civilian usage and pollution of these substances were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

The explosives related chemicals represent 9 of the 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

In the preparation of this report, several reference sources have been directly quoted. Permission has been obtained from the appropriate sources for reprint of the quoted information.

TABLE OF CONTENTS

	<u>Page</u>
Executive Summary	5
Foreword	11
I. General Overview of Explosives Manufacture, Loading and Disposal of Explosives	27
A. RDX/HMX Manufacture	27
1. Manufacturing Facilities at Holston AAP	32
2. Process Description and Effluent Streams	32
a. Reagent Preparation	34
b. Nitration of Hexamine	34
c. Acids Removal and Explosives Wash	37
d. Recrystallization	40
e. Dewatering	40
f. Incorporation	40
g. Primary Distillation and Ammonia Recovery	44
3. Characterization of Effluents from the Manufacture of RDX/HMX	47
4. Future Effluent Treatment Plans	51
B. TNT Manufacture	53
1. Manufacturing Facilities	53
2. Process Effluent Streams	54
C. Explosives Blending and Loading Operations	58
1. Explosives Blending	58
2. Explosives Loading, Assembly and Pack	58
a. Cornhusker AAP	59
b. Kansas AAP	59
c. Lone Star AAP	59
d. Louisiana AAP	59
e. Milan AAP	59
f. Iowa and Joliet AAP	59
3. Future Pink Water Treatment	60
D. Disposal of Solid Explosives Wastes	60
1. Wastes from Explosives Manufacturing	60
2. Wastes from Explosives Loading Operations	63
3. Disposal of Outdated Explosives	63
E. References	65
Hexamine	67
Summary	69
Foreword	71
Table of Contents	73

TABLE OF CONTENTS
(continued)

	<u>Page</u>
II. Hexamine	75
A. Alternate Names	75
B. Physical Properties	75
C. Chemical Properties	77
1. General Reactions	77
2. Environmental Chemistry	78
3. Detection and Analysis	79
D. Uses of Hexamine in Munitions Production	79
1. Purpose and Quantities Used	79
2. Occurrences of Hexamine in Aqueous Effluents	81
E. Uses in the Civilian Community	82
1. Production Methodology	82
2. Manufacturers, Production and Capacity	82
3. Usages	84
4. Future Trends	85
5. Documented or Speculated Occurrences in the Environment	85
F. Comparison of the Civilian and Military Uses and Pollution of Hexamine	86
G. Toxicological and Environmental Hazards	86
1. Effects of Hexamine on Man	86
2. Toxicity of Hexamine to Mammals	87
a. Acute Toxicity	87
b. Chronic Toxicity	87
c. Teratogenicity and Mutagenicity	89
d. Carcinogenicity	89
3. Aquatic Toxicity	92
4. Toxicity to Invertebrates	94
5. Microorganism Toxicity	94
6. Phytotoxicity	94
7. Environmental Fate	95
8. Availability of Literature for Phase II	95
H. Regulations and Standards	95
1. Air and Water Acts	95
2. Occupational Standards	95
3. National Cancer Institute	96
4. Department of Transportation	96
I. Conclusions and Recommendations	96
J. References	99

TABLE OF CONTENTS
(continued)

	<u>Page</u>
Cyclohexanone	103
Summary	105
Foreword	107
Table of Contents	109
III. Cyclohexanone	111
A. Alternate Names	111
B. Physical Properties	111
C. Chemical Properties	113
1. General Reactions	113
2. Environmental Reactions	115
3. Sampling and Analysis	116
D. Uses of Cyclohexanone in Army Munitions Production	117
1. Quantities of Cyclohexanone Used in Munition Production	117
2. Occurrences of Cyclohexanone in 'Air' and 'Water'	117
a. Aqueous Effluents from RDX Recrystallization (G-Buildings)	117
b. Air Effluents from the RDX Recrystallization and Formulation (G-Buildings)	119
c. Aqueous Effluents from RDX Dewatering (H-Buildings)	119
d. Holston River Concentration of Cyclohexanone	120
e. Material Balance of Cyclohexanone	120
E. Uses in the Civilian Community	120
1. Production Methodology	120
2. Manufacture, Production and Capacity	122
3. Usages	124
4. Future Trends	125
5. Documented or Speculated Occurrences in the Environment	125
F. Comparison of the Military and Civilian Uses of Cyclohexanone	126
G. Environmental and Toxicological Hazards of Cyclohexanone	126
1. Human Exposure Studies	126
2. Mammalian Toxicity	127
a. Acute and Chronic Toxicity	127
b. Teratogenicity, Mutagenicity and Carcinogenicity	127

TABLE OF CONTENTS
(continued)

	<u>Page</u>
c. Biochemistry of Cyclohexanon	130
3. Aquatic Toxicity	131
4. Phytotoxicity	133
5. Toxicity of Microorganisms	133
6. Environmental Fate	134
7. Literature Availability for Phase II	135
H. Standards and Regulations	136
1. Air and Water Acts	136
2. Occupational Standards	136
3. Department of Transportation	136
I. Conclusion and Recommendations	136
J. References	139
Methylamines	143
Summary	145
Foreword	147
Table of Contents	149
IV. The Methylamines	151
A. Introduction	151
B. Alternate Names	151
C. Physical Properties	152
D. Chemical Properties	152
1. General Reactions	152
2. Environmental Reactions	157
a. N-nitrosodimethylamine Formation	157
b. Photochemical Decomposition	162
c. Oxidation Reactions	163
3. Sampling and Analysis	163
E. Uses in Army Munitions Production	165
1. Purposes	165
2. Estimated or Speculated Occurrences in the Environment	166
F. Uses in Civilian Community	166
1. Production Methodology	166
2. Production, Manufacturers and Capacities	168
3. Usages	169
4. Future Trends	170
5. Documented or Speculated Occurrences in the Environment	170

TABLE OF CONTENTS
(continued)

	<u>Page</u>
G. Comparison of Military and Civilian Usage and Production	172
H. Toxicological and Environmental Hazards	172
1. Toxicity to Mammals	172
2. Aquatic Toxicity	175
3. Degradation of the Methylamines by Microorganisms	176
a. Biochemical Pathways for Microbial Degradation of the Methylamines to Formaldehyde and Ammonia	176
b. Formation of N-nitrosodimethylamine Microorganisms	178
4. Phototoxicity	181
5. Availability of Literature for Phase II	185
I. Regulations and Standards	185
1. Air and Water Standards	185
2. Occupational Exposure Limits	185
3. Department of Transportation	186
J. Conclusion and Recommendations	186
K. References	189
Hexahydro-1,3-dinitro-5-acetyl-s-triazine (TAX)	195
Summary	197
Foreword	199
Table of Contents	201
V. TAX - Hexahydro-1,3-dinitro-5-acetyl-s-triazine	203
A. Alternate Names	203
B. Physical Properties	203
C. Chemical Properties	204
1. Synthesis	204
2. General Reactions	205
3. Environmental Reactions	206
4. Sampling and Analysis	206
D. Uses of TAX in Munitions Production	206
1. Uses	206
2. Occurrences of TAX in the Aqueous Effluents from HAAP	207
E. Uses in the Civilian Community	207

TABLE OF CONTENTS
(continued)

	<u>Page</u>
F. Comparison of Civilian and Military Uses and Pollution of TAX	207
G. Toxicological and Environmental Hazards	209
1. Mammalian Toxicity	209
2. Aquatic Toxicity	209
3. Availability of Literature for Phase II	209
H. Regulations . Standards	209
I. Conclusion and Recommendations	209
J. References	211
 Octahydro-1-acetyl-3,5,7-trinitro-s-tetrazine (SEX)	 213
Summary	215
Foreword	217
Table of Contents	219
VI. SEX - Octahydro-1-acetyl-3,5,7-trinitro-s-tetrazine	221
A. Alternate Names	221
B. Physical Properties	221
C. Chemical Properties	222
1. Synthesis	222
2. General Reactions	222
3. Environmental Reactions	223
4. Sampling and Analysis	224
D. Uses in Army Munitions Production	224
1. Uses	224
2. Occurrences of SEX in the Aqueous Effluents from HAAP	224
E. Uses in the Civilian Community	226
F. Comparison of Civilian and Military Uses and Pollution of SEX	226
G. Toxicological and Environmental Hazards	226
1. Mammalian Toxicity	226
2. Aquatic Toxicity	227
3. Availability of Literature for Phase II	227
H. Regulations and Standards	227
I. Conclusion and Recommendations	227
J. References	229

TABLE OF CONTENTS
(continued)

	<u>Page</u>
1,3-dinitrobenzene	231
Summary	233
Foreword	235
Table of Contents	237
VII. 1,3-dinitrobenzene	239
A. Alternate Names	239
B. Physical Properties	239
C. Chemical Properties	241
1. General Reactions	241
a. Reductive Reactions	241
b. Electrophilic Substitution	242
c. Thermal Decomposition	242
2. Sampling and Analysis	243
D. Uses of 1,3-dinitrobenzene in Army Munitions Production	244
1. Purposes	244
2. Speculated or Estimated Losses of 1,3-dinitrobenzene from TNT Manufacturing	244
a. Process Losses	244
b. Production of 1,3-dinitrobenzene in the Environment	245
c. Estimated 1,3-dinitrobenzene Discharges from TNT Manufacture	245
3. Estimated or Speculated Losses from TNT Blending Operations	245
4. Estimated or Speculated Losses from LAP Operations	246
E. Uses in the Civilian Community	246
1. Production Methodology	246
2. Manufactureres, Production and Capacities	246
3. Usages	246
4. Future Trends	246
5. Documented or Speculated Occurrences in the Environment	247
F. Comparison of Military and Civilian Usages of 1,3- dinitrobenzene	247
G. Toxicological and Environmental Hazards	247
1. Human Toxicity	247
2. Toxicity to Mammals and Birds	247
a. Acute and Chronic Toxicity	247
b. Biochemistry	248

TABLE OF CONTENTS
(continued)

	<u>Page</u>
c. Mutagenicity, Carcinogenicity and Teratogenicity	248
3. Toxicity to Aquatic Organisms	248
4. Toxicity to Microorganisms	253
5. Phytotoxicity	253
6. Environmental Fate of 1,3-dinitrobenzene	255
7. Availability of Literature for Phase II	255
H. Regulations and Standards	255
I. Conclusion and Recommendations	255
J. References	257
1,3,5-trinitrobenzene	261
Summary	263
Foreword	265
Table of Contents	267
VIII. 1,3,5-trinitrobenzene	269
A. Alternate Names	269
B. Physical Properties	269
C. Chemical Properties	269
1. General Reactions	269
2. Sampling and Analysis	273
D. Uses of 1,3,5-trinitrobenzene in Army Munitions Production	274
1. Purposes	274
2. Estimated or Speculated Losses of 1,3,5-TNB from TNT Manufacture	274
a. Process Losses	274
b. 1,3,5-TNB Production in the Environment	275
c. Estimated 1,3,5-TNB Discharges from TNT Manufacture	276
3. Estimated or Speculated Losses of 1,3,5-TNB from TNT Blending Operations	276
4. Estimated or Speculated Losses of 1,3,5-TNB from LAP Operations	276
E. Uses of 1,3,5-trinitrobenzene in Civilian Community	277
1. Production Methodology	277
2. Manufacturers, Production and Capacities	277
3. Usages	277
4. Future Trends	278

TABLE OF CONTENTS
(continued)

	<u>Page</u>
5. Documented or Speculated Occurrences in the Environment	278
F. Comparison of Army and Civilian Uses of 1,3,5-TNB . . .	278
G. Toxicological and Environmental Hazards of 1,3,5-trinitrobenzene	278
1. Mammalian Toxicity	278
2. Aquatic Toxicity	280
3. Microorganism Toxicity	280
4. Phytotoxicity	282
5. Environmental Fate	282
6. Availability of Literature for Phase II	283
H. Regulations and Standards	283
I. Conclusion and Recommendations	283
J. References	285
K. Abbreviations and Symbols	289
L. Distribution List	294

LIST OF TABLES

<u>Number</u>		<u>Page</u>
S-1	Summary of Recommendations for Future Work in Explosive Related Chemicals	6
I-1	Composition of Products Formulated at Holston AAP	29
I-2	Historical Explosives Production and Projected Mobilization Production at Holston AAP	30
I-3	Summary of Historical and Projected Mobilization Usage of Explosives at Holston AAP	31
I-4	Reactants for RDX and HMX Manufacture Based on 100 lb Reactor Charge	32
I-5	Water Quality Data Summary (1976-1977) - Area B Holston AAP	49
I-6	Water Quality Data for 1977 - Area B Holston AAP	50
I-7	Comparison of the Overall Discharges Resulting from the Production of TNT by the Batch and CIL Continuous Process .	57
I-8	Performance of LAP Wastewater Treatment System at Joliet AAP	62
II-1	Physical Properties of Hexamine	76
II-2	Comparison of Current Spectrometric Analytical Methods for Formaldehyde	80
II-3	Hexamine Purchase and Concurrent RDX/HMX Production	81
II-4	U.S. Hexamine Production, 1965 to 1976 in Million Pounds .	82
II-5	Current Manufacturers of Hexamine	84
II-6	Chronic Toxicity of Hexamine on Mammals	88
II-7	Teratogenic and Mutagenic Effects of Hexamine	90
II-8	Carcinogenicity Studies with Hexamine	91
II-9	Toxicity of Formaldehyde to Aquatic Animals	93
II-10	Toxicity of Hexamine to Microorganisms	94
III-1	Physical Properties of Cyclohexanone	112
III-2	Historical Purchase of Cyclohexanone and Corresponding RDX Production at Holston AAP	117
III-3	Aqueous Effluents from Typical RDX Recrystallization Buildings	118
III-4	Aqueous Effluents from a Typical RDX Dewatering Building .	119
III-5	U.S. Cyclohexanone Production, 1965 to Present	124
III-6	Current Producers of Cyclohexanone	124
III-7	Acute Toxicity of Cyclohexanone to Mammals	128

LIST OF TABLES
(continued)

<u>Number</u>		<u>Page</u>
III-8	Chronic Toxicity of Cyclohexanone	129
III-9	Excretion of Glucuronic Acids and Sulfates in 24 Hour Urine Samples of Rabbits Following Oral Administration of Cyclo- hexanone	131
III-10	Acute Toxicity of Cyclohexanone to Aquatic Organisms . . .	132
III-11	Cyclohexanone Levels in the Holston River	133
IV-1	Physical Properties of Methylamine, Dimethylamine and Trimethylamine	153
IV-2	Yields of N-nitrosodimethylamine at 100°C and at Different pH Values	158
IV-3	Formation of N-nitrosodimethylamine from Trimethylamine or Trimethylamine Oxide and Nitrite in Acetic Acid	159
IV-4	Amounts of N-nitrosodimethylamine Formed from Equimolar Amounts of Dimethylamine and Trimethylamine	160
IV-5	Amount of N-nitrosodimethylamine Formed from Equimolar Amounts of Trimethylamine and Dimethylamine at Different Acidities and Temperatures	161
IV-6	Levels of the Methylamines in Arnott Branch as a Function of Different Degrees of Mixing	166
IV-7	U.S. Producers of Methylamines	168
IV-8	Uses of Methylamines	170
IV-9	Dimethylamines in Foodstuffs and Tobacco	171
IV-10	Acute Toxicity of the Methylamines to Mammals	173
IV-11	Acute Toxicity of the Methylamines to Aquatic Organisms . .	175
IV-12	N-nitrosodimethylamine Production by Various Bacteria . . .	180
IV-13	Quantity and Quality of Effluents Which May Be Discharged from the Manufacture of the Methylamines	185
V-1	Physical Properties of TAX	203
V-2	Analysis of Waste Streams for RDX, HMX and TAX	208
VI-1	Physical Properties of SEX	221
VI-2	Analysis fo Waste Streams for RDX, HMX, TAX and SEX	225
VII-1	Physical Properties of 1,3-dinitrobenzene	240
VII-2	Estimated Discharges and River Concentrations of 1,3-DNB at Full TNT Production	245

LIST OF TABLES
(continued)

<u>Number</u>		<u>Page</u>
VII-3	Acute Effects of 1,3-dinitrobenzene on Animals	249
VII-4	Metabolites of m-dinitro[¹⁴ C]benzene Excreted in Urine by Rabbits	250
VII-5	Effect of 1,3-dinitrobenzene on Aquatic Organisms	252
VII-6	Growth Inhibition of Bacteria and Fungi by 1,3-dinitrobenzene	254
VIII-1	Physical Properties of 1,3,5-trinitrobenzene	270
VIII-2	Estimated Discharges and River Concentrations of 1,3,5-TNB at Full TNT Production	276
VIII-3	Acute and Chronic Animal Toxicity of 1,3,5-trinitrobenzene	279
VIII-4	Effect of 1,3,5-trinitrobenzene on Aquatic Organisms	280
VIII-5	Growth Inhibition of Bacteria and Fungi by 1,3,5-TNB	281
VIII-6	Concentration of Nitrobenzenes Required for 50% Inhibition of Growth Rate of <i>Trichoderma viride</i>	282

LIST OF FIGURES

<u>Number</u>		<u>Page</u>
I-1	Map of the Holston Army Ammunition Plant Area	28
I-2	Detailed Map of Area B, Holston AAP	33
I-3	Flow Diagram of the RDX/HMX Manufacture at Holston AAP . .	35
I-4	Preparation of Hexamine/Acetic Acid in Building C-5	36
I-5	Nitration of Hexamine	38
I-6	Acids Removal and Explosives Wash in Building E-8	39
I-7	RDX/HMX Recrystallization in Building G-8	41
I-8	Dewatering, Filtration and Grinding of RDX/HMX in Building H-6	42
I-9	Incorporation and Drying in Buildings I, J, L and M	43
I-10	Primary Distillation of Spent Acid in Building B-11	45
I-11	Ammonia Distillation in Building A-1	46
I-12	Manufacture of TNT by the Batch Process	55
I-13	Manufacture of TNT by the CIL Continuous Process	56
I-14	Schematic of Carbon Adsorption Treatment of Pink Water at LAP Plants	61
II-1	Infrared Spectrum of Hexamine	77
II-2	Manufacture of Hexamethylenetetramine	83
III-1	Infrared Spectrum of Cyclohexanone	111
III-2	Ultraviolet Spectrum of Cyclohexanone	113
III-3	Production of Cyclohexanone by the Air Oxidation Process .	121
III-4	Production of Cyclohexanone by Hydrogenation of Phenol . .	123
IV-1	Infrared Spectra of the Methylamines	154
IV-2	Ultraviolet Spectra of the Methylamines	155
IV-3	Nucleophilic Addition Reactions of the Methylamines	156
IV-4	Oxidative Degradation Reactions of the Methylamines	164
IV-5	Production of the Methylamines	167
IV-6	<i>In vivo</i> Metabolic Scheme for the Methylamines	174
IV-7	Oxidation of Trimethylamine by Obligate and Facultative Methylotrophs	177
IV-8	The Oxidation of N-methyl Compounds to Formaldehyde	179
IV-9	N-nitrosodimethylamine Formation in Sewage	182

LIST OF FIGURES
(continued)

<u>Number</u>		<u>Page</u>
IV-10	Formation of N-nitrosodimethylamine in Samples of Lake Water of Differing Acidities	183
IV-11	Formation of N-nitrosodimethylamine in Sterile and Nonsterile Langford Soil	184
V-1	Ultraviolet Spectrum of TAX	204
VI-1	Ultraviolet Spectrum of SEX	222
VII-1	Infrared Spectrum of 1,3-dinitrobenzene	239
VII-2	1,3-dinitrobenzene Metabolic Pathway in Rabbits	251

I. GENERAL OVERVIEW OF EXPLOSIVES MANUFACTURE, LOADING AND DISPOSAL OF EXPLOSIVES

A. RDX/HMX Manufacture

Several of the explosives-related chemicals to be evaluated in this preliminary problem definition study are associated with the manufacture of RDX and HMX. These chemicals include:

- hexamine - a starting material
- cyclohexanone - a recrystallization solvent
- the methylamines, TAX and SEX - process by-products

At the present time RDX and HMX are manufactured exclusively at Holston Army Ammunition Plant (HAAP). The plant is located in Kingsport, Tennessee on the Holston River as shown in Figure I-1. Because of the increased usage of RDX explosive mixtures, a second plant to produce these explosives will be constructed in the future. This new facility (X-facility) is currently in the planning stages. Final site selection and authorization of construction funds have not been completed.

Both RDX and HMX are used in a large number of explosive mixtures which have a variety of end uses. The formulations of some of these explosive mixtures are presented in Table I-1. Formulations of RDX and desensitizing waxes are designated as the Composition A explosives. These mixtures are used in press loaded small artillery shells. A-3 and A-5 are also used as booster charges in place of tetryl which is no longer manufactured by the Army.

Composition B and cyclotols are mixtures of RDX and TNT. Desensitizing wax is also added to the Composition B products. The octols are HMX and TNT mixtures. These compounded explosives exhibit superior performance properties over that of TNT alone. The superior properties have lead to the extensive use of Composition B as burster charges in bombs, artillery shells and land mines. For this purpose, the Composition B explosive is melt-loaded into the shells. Once solidified, the cast explosive can be drilled for insertion of non-bursting charge components. Because of its wide use in shells and bombs, Composition B utilizes ~ 75% of the RDX produced each year.

A third major group of explosive mixtures containing RDX and HMX are the plastic explosives and demolition charges. These formulations are known as the Composition C, PBX and PBXN explosives and contain RDX or HMX compounded with plastizers and solvents. In addition to its use in explosive mixtures, HMX is also used in solid rocket propellants.

The historical production figures for these explosives are presented in Table I-2. The quantities of the explosive which would be produced at full mobilization are also shown in this Table. A summary of the historical and projected full mobilization usage of explosives at Holston AAP is presented in Table I-3.

Figure I-1. Map of the Holston Army Ammunition Plant Area
(Small and Rosenblatt, 1974).

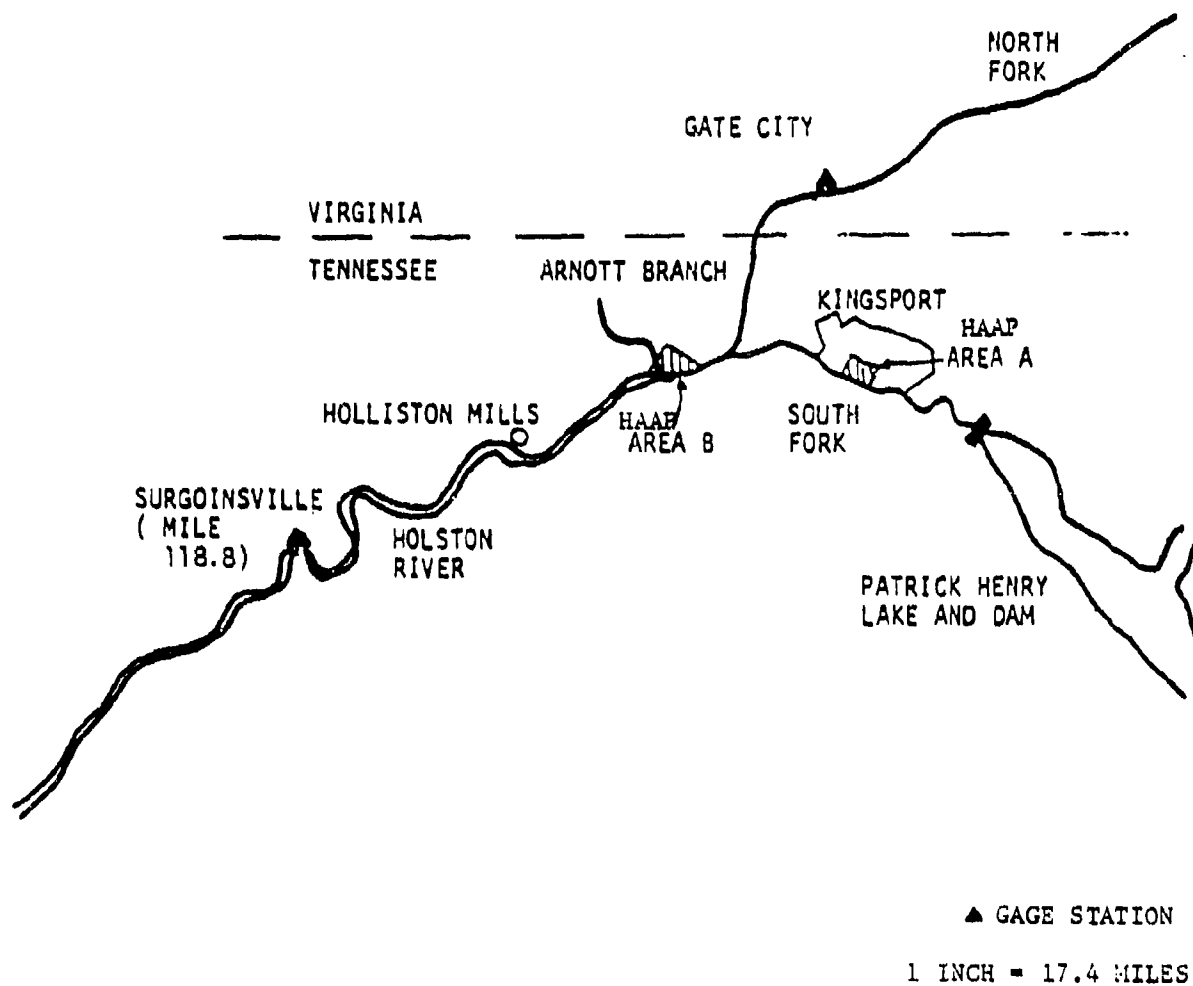


Table I-1. Composition of Products Formulated
at Holston AAP.

Product	Percentage Composition			
	RDX	HMX	TNT	Other
Desensitized RDX	96±0.3			Process Oil 4±0.5
Composition A Products				
A-3	91±0.7			Desensitizing wax 9±0.7
A-4	97±0.5			Desensitizing wax 3±0.5
A-5	98.8±0.3			Stearic acid 1.2±0.3
A-7	98.3±0.5			Desensitizing wax 1.7±0.5
Composition B Products				
B, Type I	59.5±2		39.5±2.3	Desensitizing wax 1.0±0.3
B-4, Type I	60±2		39.5±2.15	Calcium silicate 0.5±0.15
B-4, Type II	60±2		40±2	
Composition C Products				
C-4, Classes 1&2	91±1			Binder ¹ 9±1
C-4, Class 3	90±1.2			Binder ¹ 9.5±0.7
C-4, Class 4	89.9±1			Binder ¹ 10.0±1
CH-6	97.5±0.5			Dye Composition ² 0.2±0.2
				Calcium silicate 1.5±0.15
Cyclotols Products				
Cyclotol, Type I	73±2		25±2	
Cyclotol, Type II				
Class A	70±2		30±2	
Cyclotol, Type II				
Class B	69.6±2		29.9±2.15	Calcium silicate 0.5±0.15
NMX Products				
HMX, Grade A	7	93		
HMX, Grade B	2	98		
CHX-1 or 2		92.2±0.5		Laminac EPX-147-1 or 147-3 7.8±0.5
HMX/KEL-F		95±0.4		KEL-F 5±0.4
LX-04-1		85±1		Viton A incl. GAF perm. yellow & GR Toner 12-500 15±1
LX-10-1		94.5±0.5		Viton A incl. Cyan Green Toner 12-3100 5±0.5
LX-14-0		95.5±0.5		Estane 5702-F-1 plus Hallowen Violet Toner 4.5±0.5
Octol, Type I		75±2	25±2	
Octol, Type II		70±2	30±2	
PBX Products				
PBX, Type I	90±0.5			Polystyrene 8.5±0.3
				Di-2-ethylhexyl phthalate 1.5±0.3
PBX, Type II	90±0.5			Polystyrene 9.1±0.2
				Di-2-ethylhexyl phthalate 0.5±0.1
				Gum Rosin incl. Naphthol Red 0.4±0.1
PBX 9404		94±0.5		Nitrocellulose 3
				CEP (Fyrol) 3
PBX 9501		95±0.5		Diphenylamine 0.1±0.01
PBXN-3		86±0.5		Binder ³ 5.0±0.5
PBXN-5		95.5±0.5		Nylon 14±0.5
PBXN-6	95±0.5			Copolymer ⁴ 5±0.5
PBX 9010	90±0.5			Copolymer ⁴ 5±0.5
PBX 9011	90±0.5			KEL-F 10±0.3
PBX 9203	92±0.5			Estane 5703F-1 10±0.5
				Polystyrene 6±0.4
				Di-2-ethylhexyl phthalate 2±0.1
PBX 9407	94±0.5			Exxon 461 6±0.4
PBX 9502				TATB 95±0.3
				KEL-F 5±0.3
PBX 0280	95±0.4			Estane 5703 F-1 5±0.8

1. polyisobutylene and di-2-ethyl sebacate or di-2-ethyl adipate
2. 90% lead chromate, 10% lamp black
3. Estane 5703 F-1 plastic and bis(2,2-dinitropropyl) acetate/bis(2,2-dinitropropyl) formal
4. Vinylidene difluoride and hexafluoropropylene

Table I-2. Historical Explosives Production and Projected Mobilization
Production at Holston AAP in 1000 lb.

	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	Full Mobilization
Composition B	218,900	272,223	249,477	168,660	158,755	152,105	165,808	138,993	61,447	28,111	10,491	264,456
Desensitized RDX	2,041	1,791	2,152	1,785	3,645	-	-	-	-	-	-	-
RDX - Type B	164	169	32	18	27	122	547	726	543	-	-	-
RDX - Type P	1,069	210	-	-	-	-	-	15	283	13	49	-
Composition A-3	986	6,327	10,368	3,952	1,451	2,411	4,660	4,308	3,219	5,896	2,430	21,732
Composition A-4	1,005	597	530	762	547	119	109	-	-	98	145	3,768
Composition A-5	-	1,988	1,156	1,161	1,751	1,481	2,334	2,386	787	579	1,662	73,404
Composition B-3	150	51	-	-	-	-	-	-	-	-	-	-
Composition B-4	11,609	10,680	21,460	16,458	9,897	2,645	3,468	3,637	1,375	77	413	-
Composition C-4	6,373	11,184	6,860	4,650	4,661	2,475	2,579	1,978	1,670	-	137	6,060
Cyclotol	16,990	18,747	23,382	10,014	2,032	2,297	4,971	4,522	2,765	22	87	10,932
Octol	1,455	2,163	3,231	2,863	1,533	3,262	5,387	2,288	2,156	382	441	1,620
RDX, Grade II All Classes	522	133	414	473	597	685	655	91	21	23	34	1,908
CS-1	401	421	101	3	-	46	74	-	-	22	28	-
PB-IX-UG-1	52	-	-	11	10	135	83	131	78	-	-	-
PB-RMX 9404	315	40	114	92	67	63	85	22	73	-	-	240
Misc. RDX's	25	42	882	897	128	176	272	194	129	39	141	-
Misc. RDX's	40	22	620	70	128	516	276	787	857	1,101	1,906	-
Misc. PBX's	14	130	43	58	42	34	54	264	220	169	85	-
Other	64	-	14	-	-	1,443	48	7,448	17,353	16,479	2,530	-

Table I-3. Summary of Historical and Projected Mobilization Usage
of Explosives at Holston AAP in 1000 lb.

Product	RDX and/or RDX Content	TNT Content	10 Year Total Production	RDX and/or RDX Used	TNT Used	10 Year High	10 Year Low	Production at Full Mobilization	RDX to be Used	TNT to be Used
Composition B	60	40	1,605,160	963,096	642,064	272,223	10,691	264,456	158,676	105,782
Emulsitized RDX	96		11,514	11,053	-	3,645	0			
RDX, Type II	100		3,987	3,987		1,233	13			
Composition A-3	91		44,943	46,903		10,358	986	21,732	19,776	
Composition A-4	97		3,992	3,872		1,045	0	5,368	3,655	
Composition A-5	98.5		15,485	15,253		2,386	0	13,404	13,203	
								45,464CH6		
Composition B-3	60	40	201	121	80	150	0			
Composition B-4	66	40	81,679	49,007	22,671	21,460	37			
Composition C-4	50		42,567	36,310		11,184	0	6,060	5,454	
Cyclotol	70	30	86,429	60,500	25,929	23,382	27	10,932	7,452	4,373
Detol	70	30	25,141	17,599	7,542	5,387	382	1,620	1,134	486
RDX Grade II	100		3,648	3,648		685	21	1,908	1,908	
CXA-1	92		1,086	999		42	0			
7B-LJ-04-1	85		490	417		131	0	240 PAX M-5	206	
PB RDX 9604	94		871	819		315	0			
Misc RDX	~ 95		2,925	2,779		897	25			
Misc RDX	~ 95		4,323	6,007		1,906	22			
Misc PEX	~ 85		1,113	946		264	14			
Others	~ 90		45,379	40,841		17,353	0			
Totals			1,982,936	1,260,157	708,286			324,120	211,660	110,641

1. Manufacturing Facilities at Holston AAP

HAAP is physically divided into two areas, Area A and Area B. Area A is the acetic acid recovery area located on the South Fork of the Holston River. In this area, dilute acetic acid from the explosives manufacture (Area B) is concentrated by azeotropic distillation. A portion of the concentrated acetic acid is then used to produce acetic anhydride. Both the acetic acid and acetic anhydride are tanked back to Area B.

Area B is located ~ 1 mile below the junction of the North and South forks of the Holston River. The explosives manufacture and compounding and the nitric acid recovery operations are located in Area B. The use of and pollution associated with the compounds of concern to this study occur in Area B. Therefore, process description and discussion of the polluting streams will be limited to the explosive area.

2. Process Description and Effluent Streams

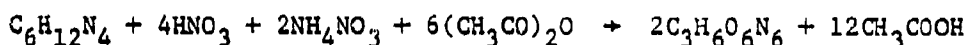
RDX and HMX are produced in the Area B buildings by the Bachmann process (Bachmann and Sheehan, 1949). A detailed map of the Area B buildings is presented in Figure I-2. In this process, hexamine is nitrated with ammonium nitrate/nitric acid mixture in an acetic acid/acetic anhydride solvent. The processing steps and the starting chemicals used in both RDX and HMX manufacture are the same. However, the proportions of materials differ as shown in Table I-4.

Table I-4. Reactants for RDX and HMX Manufacture Based on 100 lb Reactor Charge (Small and Rosenblatt, 1974).

<u>Reactant</u>	<u>Lb of Reactant for RDX Manufacture</u>	<u>Lb of Reactant for HMX Manufacture</u>
Ammonium nitrate	17.2	} 11.0
98% Nitric acid	13.6	
Hexamine	9.2	17.0
Acetic acid	15.0	18.0
Acetic anhydride	45.0	54.0

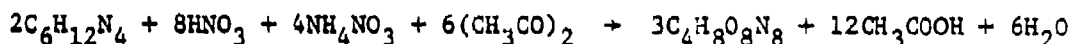
The nominal stoichiometric reactions for the formation of RDX and HMX are

RDX



Hexamine	Nitric	Ammonium	Acetic		
	Acid	Nitrate	Anhydride	RDX	Acetic
					Acid

HMX



Hexamine	Nitric	Ammonium	Acetic		
	Acid	Nitrate	Anhydride	HMX	Acetic
					Acid

Holston has ten RDX/HMX lines capable of producing $\sim 2.5 \times 10^8$ lb/yr of RDX and 1.5×10^7 lb/yr HMX at full mobilization. Currently, HAAP is only operating at $\sim 8\%$ capacity (less than full capacity on one line). A process flow diagram of the RDX/HMX manufacture is presented in Figure I-3. This process involves 6 steps which are described in detail in the following sections and Figures I-4 to I-9. Material balances on these processes have been attempted. For further information the reader is referred to Heidelberger (1971).

a. Reagent Preparation

The C Buildings are used for reagent preparation. Each C Building feeds two production lines. In these Buildings, the commercially purchased hexamine is dissolved in glacial acetic acid received from the Area A azao stills. The solution is dumped into a storage tank, the contents of which are continuously circulated through a distribution loop. The hexamine/acetic acid solution is drawn from this loop into the D Buildings as needed. The ammonium nitrate/nitric acid solutions from Building 330 are also unloaded at the C Buildings and placed in storage tanks. A schematic of the C Building operations is shown in Figure I-4.

The main discharges from the C Buildings are dissolver vent discharges and building washwater containing hexamine and dilute acids. According to a study performed by Holston Defense Corporation, an average of 30 lbs per day of hexamine is discharged from each operating C Building (USAEHA, 1971). The amount of acids and other organics was found to be negligible. The loss of hexamine was due mainly to spillage and, therefore, is relatively independent of production rates. At full mobilization, three C buildings would be mixing hexamine. Thus, ~ 90 lb/day of hexamine would be discharged to the sewer from this source.

b. Nitration of Hexamine

Nitration of hexamine is carried out in the D Buildings. RDX is produced in Buildings D-1, D-2, D-3, D-7, D-8, D-9 and D-10. These buildings each contain two continuous production units. The reactant

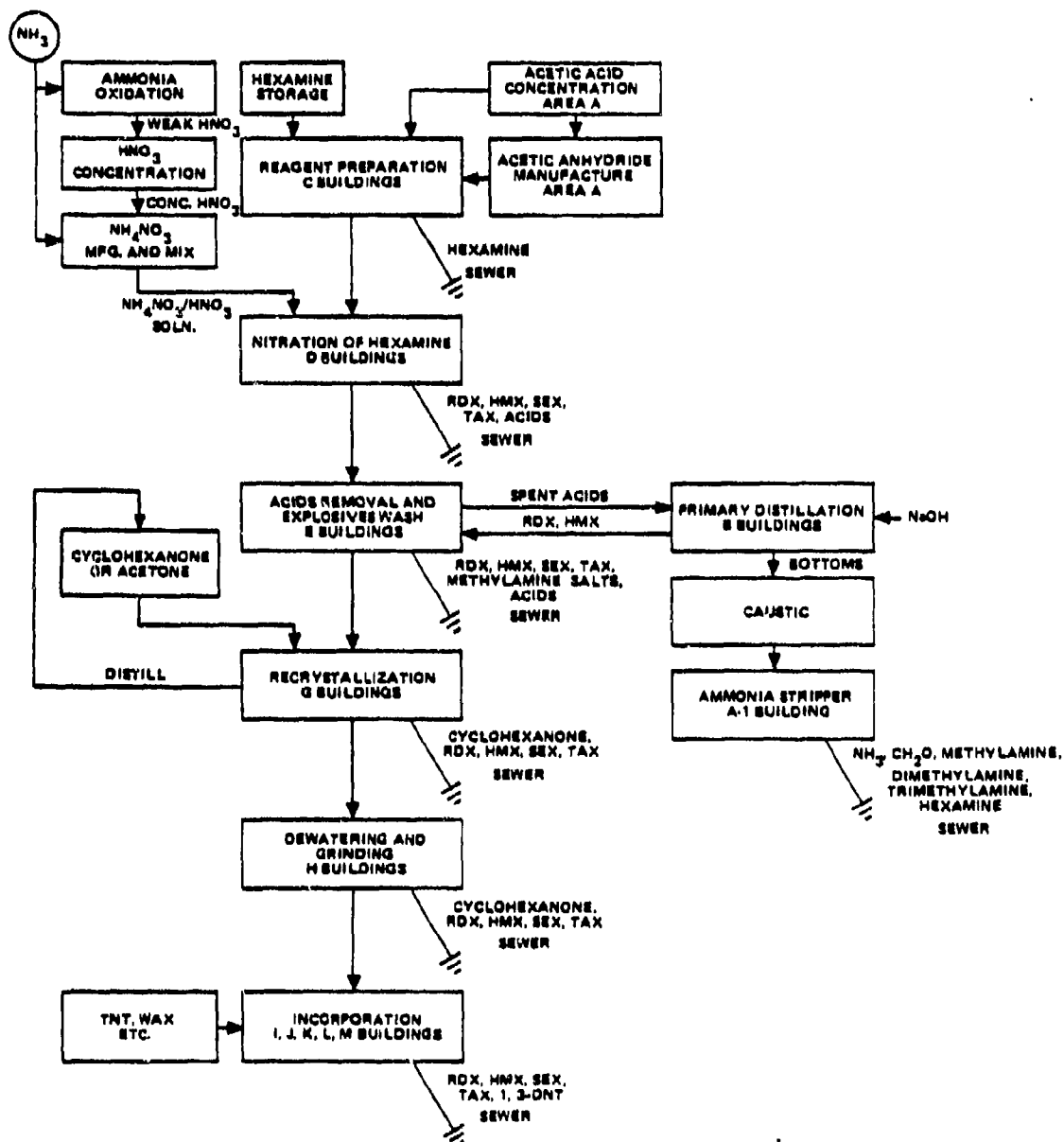


Figure I-3. Flow Diagram of the RDX/HMX Manufacture at Holston AAP.

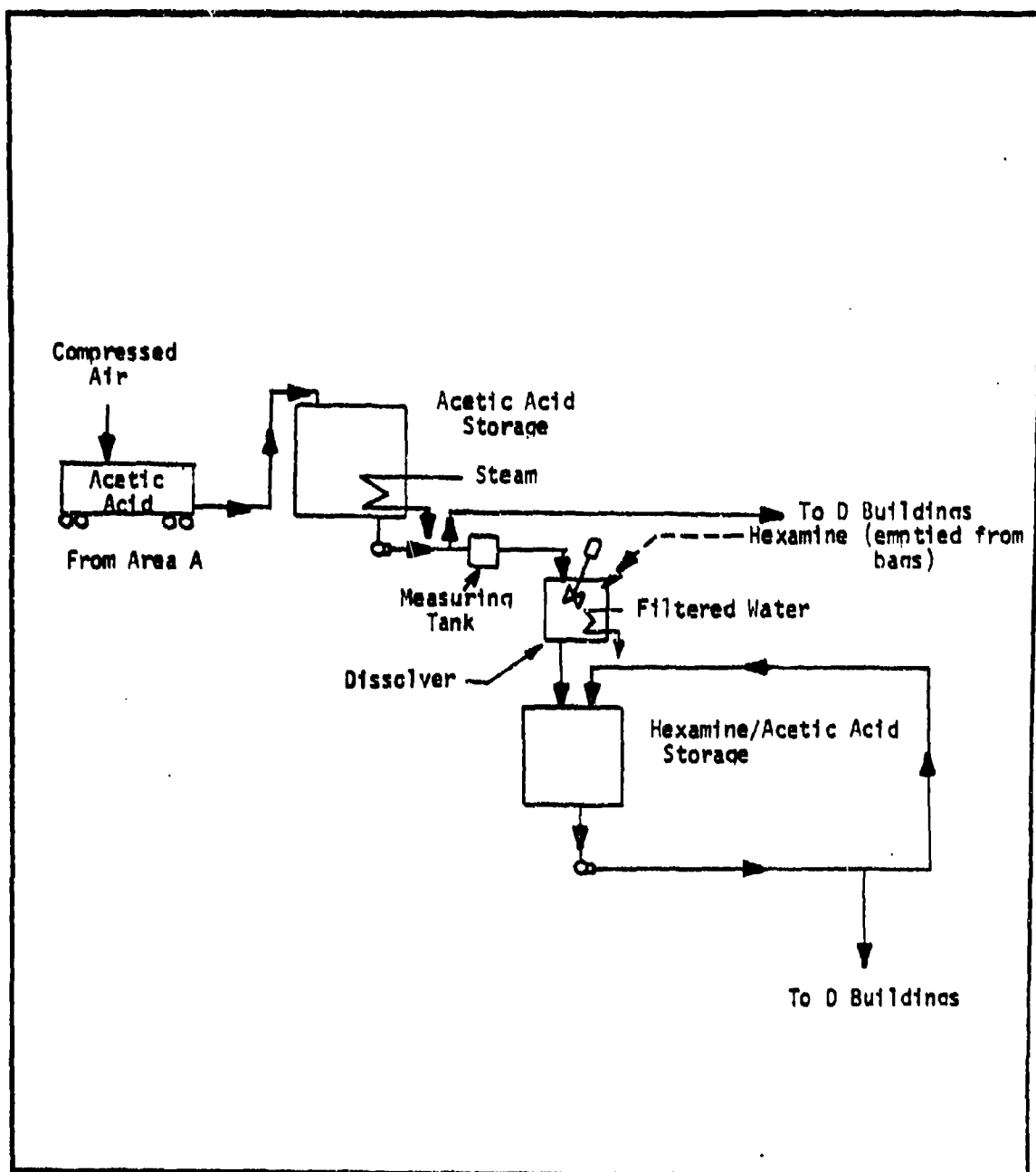


Figure I-4. Preparation of Hexamine/Acetic Acid in Building C-5 (USAEHA, 1971).

solutions - hexamine/acetic acid, nitric acid/ammonium nitrate, acetic acid and acetic anhydride are charged into the reactor at 75°C as shown in Figure I-5. The exothermic reaction is maintained under control by means of a heat exchanger. The initial product is ~ 79% RDX, 6% HMX and intermediates - the major one of which is BSX ($\text{CH}_3\text{COOCH}_2\text{-N}(\text{NO}_2)\text{-(CH}_2)_2\text{-N-NO}_2$) (Small and Rosenblatt, 1974). The reactor slurry is then pumped to a temperature controlled aging tank. Here the intermediates are further reacted to RDX. The slurry is then drained into a series of four simmer tanks where the acetic acid is diluted to 65% and the temperature is gradually lowered from 108°C to 50°C (USAEHA, 1971).

Buildings D-5 and D-6 contain batch reactors for the production of HMX. Building D-6 has two reactors and Building D-5 has one nitration reactor. These Buildings differ from the continuous RDX D Building in two respects as shown in Figure I-5:

- there is no heat exchanger on the nitrator
- each nitrator has two simmer tanks in parallel instead of four in series.

The main pollution sources from the D Buildings are the building scrubber vents, the main water effluent entering the catch basin and the various storage tank effluents (Heidelberger, 1971). Some acids and explosives are found in the effluent from equipment and floor washdown. SEX and TAX are also probably in this waste stream.

c. Acids Removal and Explosives Wash

After the nitration is completed, the explosives slurry is pumped to the E Buildings. A schematic of the E Buildings operations is presented in Figure I-6. Here the acids are removed from the slurry by a vacuum system. The acids are sent to the B Buildings where acids and dissolved explosives are recovered. Explosives recovered at the B Buildings are returned to the E Buildings for reprocessing. Once the acid has been removed, the explosive is washed with filtered water and a vacuum system is used to remove the dilute acid water. The water from this step is pumped to the D Buildings as a dilution liquor. The washed explosives are then slurried with filtered water and pumped to the G Buildings.

Buildings E-1 through E-4 and E-7 through E-10 are used for RDX production. HMX is washed in Buildings E-5 and E-6. Discharges from the E Buildings include filtered water, steam condensate and river water. Acids and explosives are discharged from the warm water wash, acid and dilution liquor receiving steam jets and equipment and floor washdowns. With the exception of the acid receiver steam jets, all the explosives containing streams flow through baffled catch drains before entering the industrial waste sewer. Most of the explosives settle out in the catch basins and do not enter the industrial sewer system. However, the water solubles such as the methylamine salts, SEX and TAX are not removed from the waste water and thus enter the sewer system.

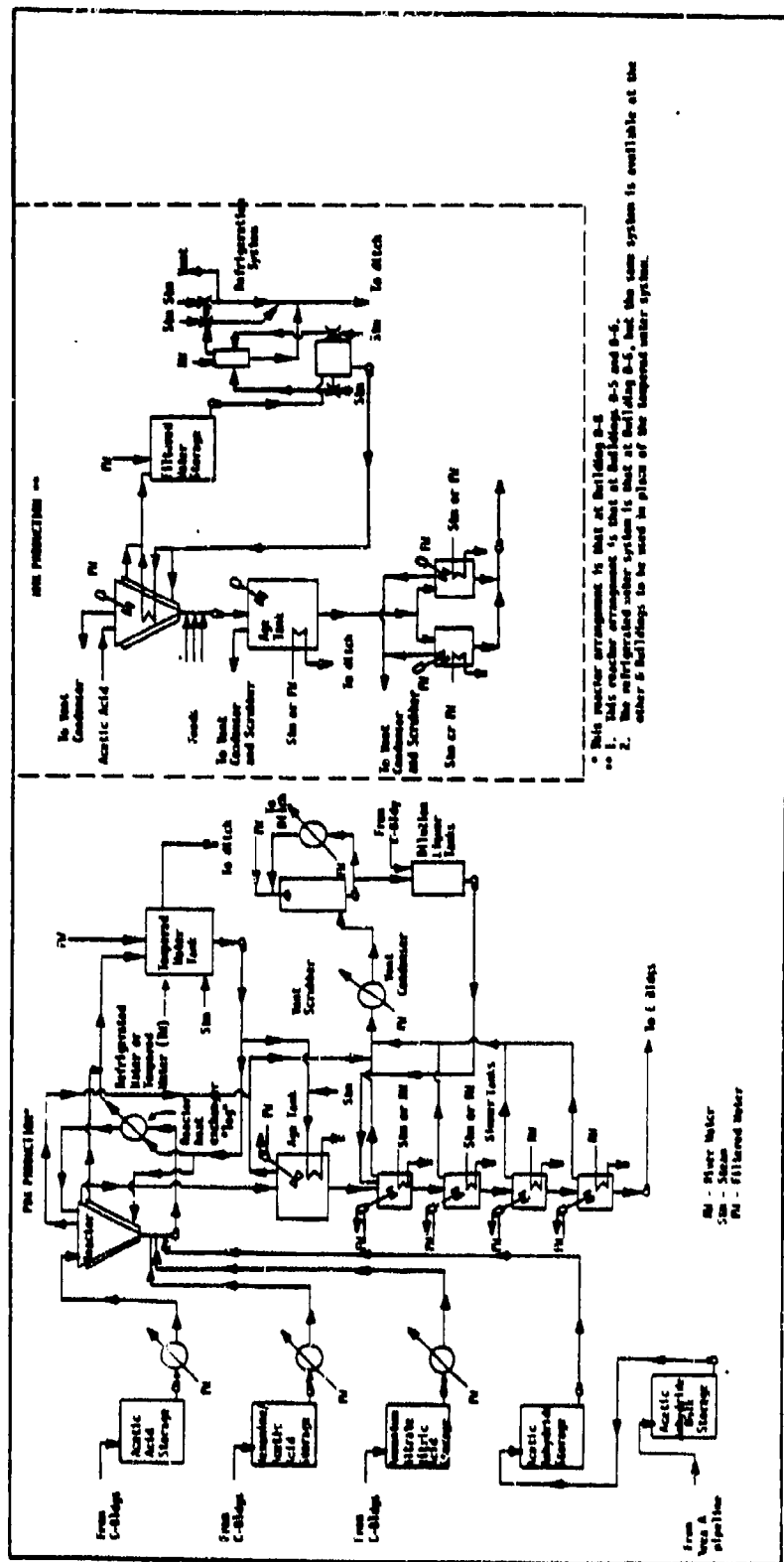


Figure I-5. Nitration of Hexamine (USAEMA, 1971).

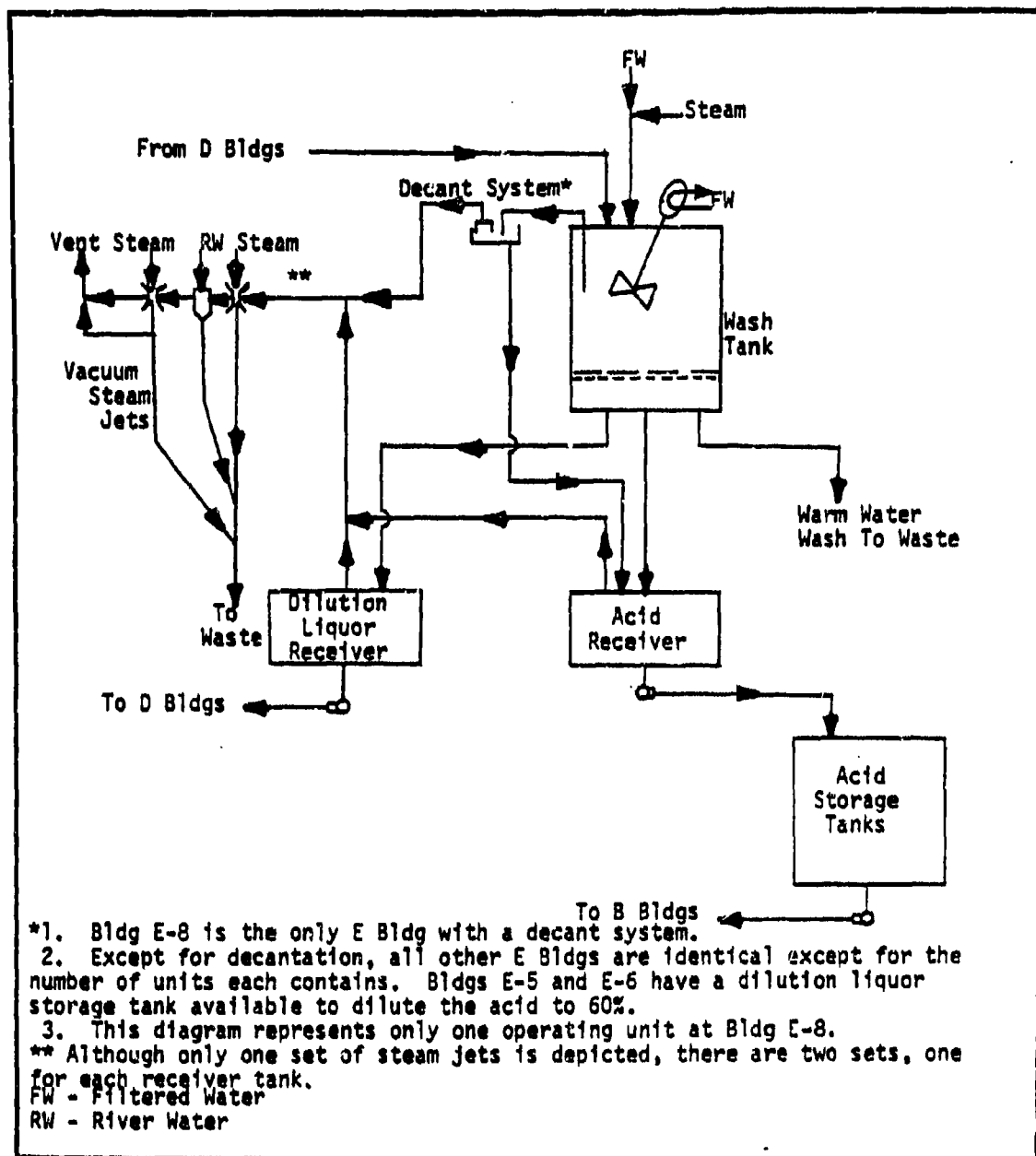


Figure I-6. Acids Removal and Explosives Wash in Building E-8 (USAEHA, 1971).

d. Recrystallization

Crude RDX or HMX from the E Buildings are recrystallized in the G Buildings. The explosive slurry is fed into a dissolver containing solvent, usually cyclohexanone for RDX and acetone for HMX. After simmering, the dissolver contents are transferred to a preheated still where the solvent is distilled off (see Figure I-7). The solvent is returned to the dissolver or a decanter. Solvent vapors from either the primary condenser or dissolver are condensed in a secondary condenser and returned to the dissolver. The recrystallized explosives are then cooled and sent to the H Buildings for dewatering.

The main pollution from the G Buildings RDX recrystallization results from the dissolver and still agitators seal water (Buildings G-1, 2, 7, 8, 9, 10, 10A). Approximately 200 ppm of cyclohexanone was found in the catch basin effluent from these buildings (USAHA, 1971). Flow rates of 27,400 gallons per day were measured.

Buildings G-3, 4, 5 and 6 are used for HMX recrystallization or special products formulation. Cyclohexanone in the 200+ ppm range is also an effluent from these G Buildings. However, the amount depends heavily upon the product being formulated. Explosives are also found in large concentrations in the effluents from all G Buildings.

e. Dewatering

After recrystallization, the explosives slurry is sent to the H Buildings for dewatering, although dewatering can also be performed in some of the G Buildings. As shown in Figure I-8, the slurry is dropped into receiving carts called nutsches. Vacuum probes are inserted into the slurry until the water is removed. Grinding of explosives is accomplished by cycling the slurry through pumps filtered with an orifice on the pump discharger or with a Cowles dissolver.

In a study conducted by Mr. Jim Green of HDC (USAHA, 1971), the principal sources of waterborne wastes from the H Buildings were determined to be from spills, and overflows of settling and vacuum tanks. Cyclohexanone is one of the wastes from these buildings (~140 ppm in a 34,800 gallon per day flow through the catch basins of each building).

f. Incorporation

In the I, J, K, L and M buildings, the wet RDX is incorporated into explosives. There are two process lines in each building. Each line has two incorporation kettles, one holdup kettle, a casting pot and a casting belt as shown in Figure I-9. The wet RDX is received in nutsches from the G buildings. Weighed quantities of dry TNT are received in melt kettles from the K buildings. Steam lines are attached to the melt kettles and the TNT melted. The hot TNT is then poured into the incorporation kettle. The wet RDX is shoveled into the kettle. The water floats to the

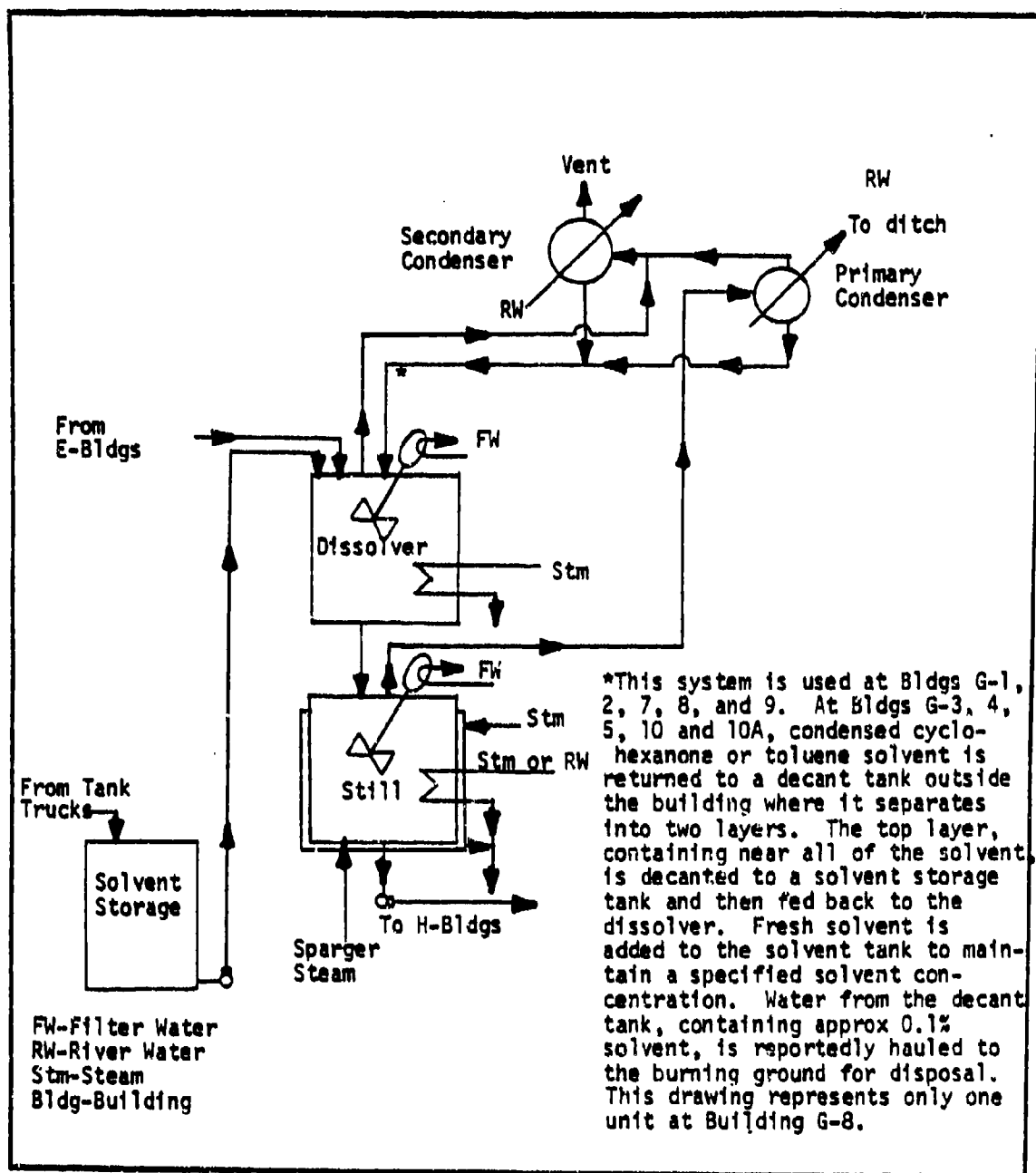
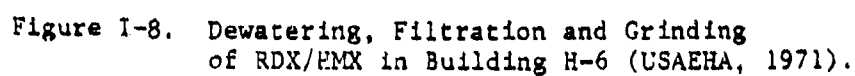


Figure I-7. RDX/HMX Recrystallization in Building G-8 (USAEHA, 1971).



top of the explosive melt and is decanted into the sewer. After removal of the water, the temperature of the melt is raised, desensitizing wax is added and the mixture agitated. After agitation the mixture is poured into a holdup tank. From the holdup tank the explosive melt flows into a casting pot, through holes in the pot and onto a casting belt. On this belt, the melt cools and solidifies. The strands of explosives fragment as they drop into nutsches. They are transported in these nutsches to the N buildings for packaging.

Water wastes from incorporating kettles and from equipment and floor wash down are the main sources of pollution from the incorporation building. This water flows through catch basins where most of the explosives are settled out. However, explosives and explosive impurities enter the main sewer system from these buildings. The amount entering the sewer is thus a function of the solubility of the explosives and impurities. Because of their higher water solubility, SEX, TAX, 1,3-DNB and 1,3,5-TNB are found in significant quantities in water from the Incorporation Buildings.

g. Primary Distillation and Ammonia Recovery

Several of the chemicals which are being evaluated during this preliminary problem definition study are by-products of the RDX-HMX manufacture. These chemicals not only appear in waste effluent streams from the main process but also in effluents from the associated reagent recovery processes. Of prime concern are the primary distillation of the contaminated weak acids from Building E and the ammonia recovery operations. Since only these two auxiliary processes are directly involved with the chemicals in this study, only these processes will be described in this report.

The contaminated weak acid from the E (acid removal) Buildings is first neutralized with 50% sodium hydroxide and then fed into a primary evaporator as shown in Figure I-10. Here ~ 80% of the original feed is recovered as 60% aqueous acetic acid. The sludge is removed, diluted with water and then heated to 100°C. The liquid is then cooled to 30°C and a RDX seed added. The precipitated RDX-HMX is separated from the solution and returned to the E Buildings. The liquid is fed to a second evaporator and a stripping column where additional acetic acid is removed.

The sludge from the stripping column is fed into a batch reactor where 50% NaOH is added. This treatment converts the ammonium nitrate into sodium nitrate and ammonia, the acetic acid to sodium acetate and the RDX-HMX to ammonia and sodium nitrate. The ammonia and water vapor released are condensed. The sludge from this reactor is pumped into storage lagoons. This sludge will be used for fertilizer production when the fertilizer plant becomes operational.

The aqueous ammonia is then distilled at Building A-1 to recover anhydrous ammonia for sale as a fertilizer (Figure I-11). The feed stream to this column contains ammonia, methyl-, dimethyl- and trimethyl-amine, formaldehyde and water. Sodium hydroxide is added to prevent corrosion (Campbell, 1976). In the presence of a base catalyst at high tempera-

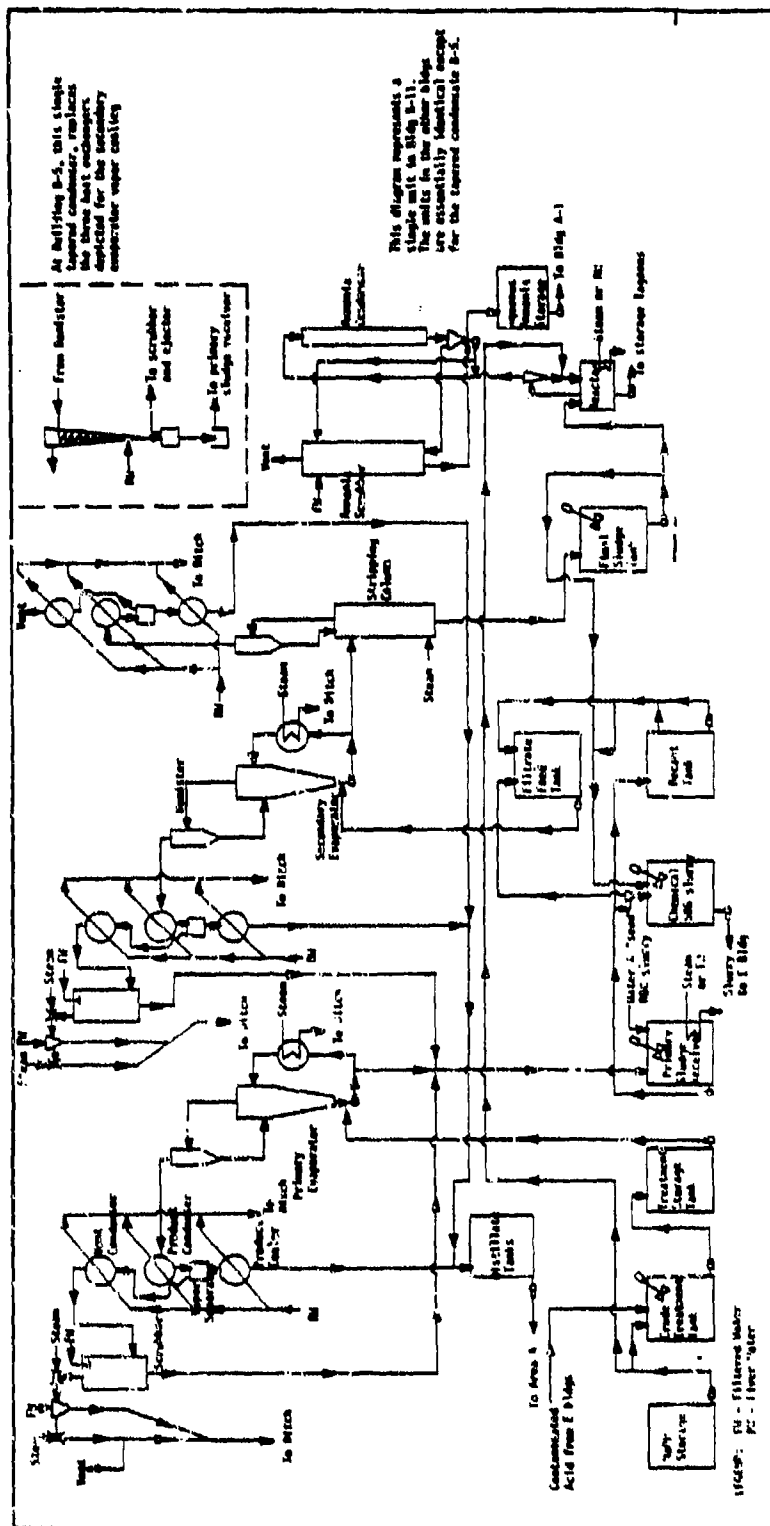


Figure I-10. Primary Distillation of Spent Acid
in Building B-11 (USAEHA, 1971).

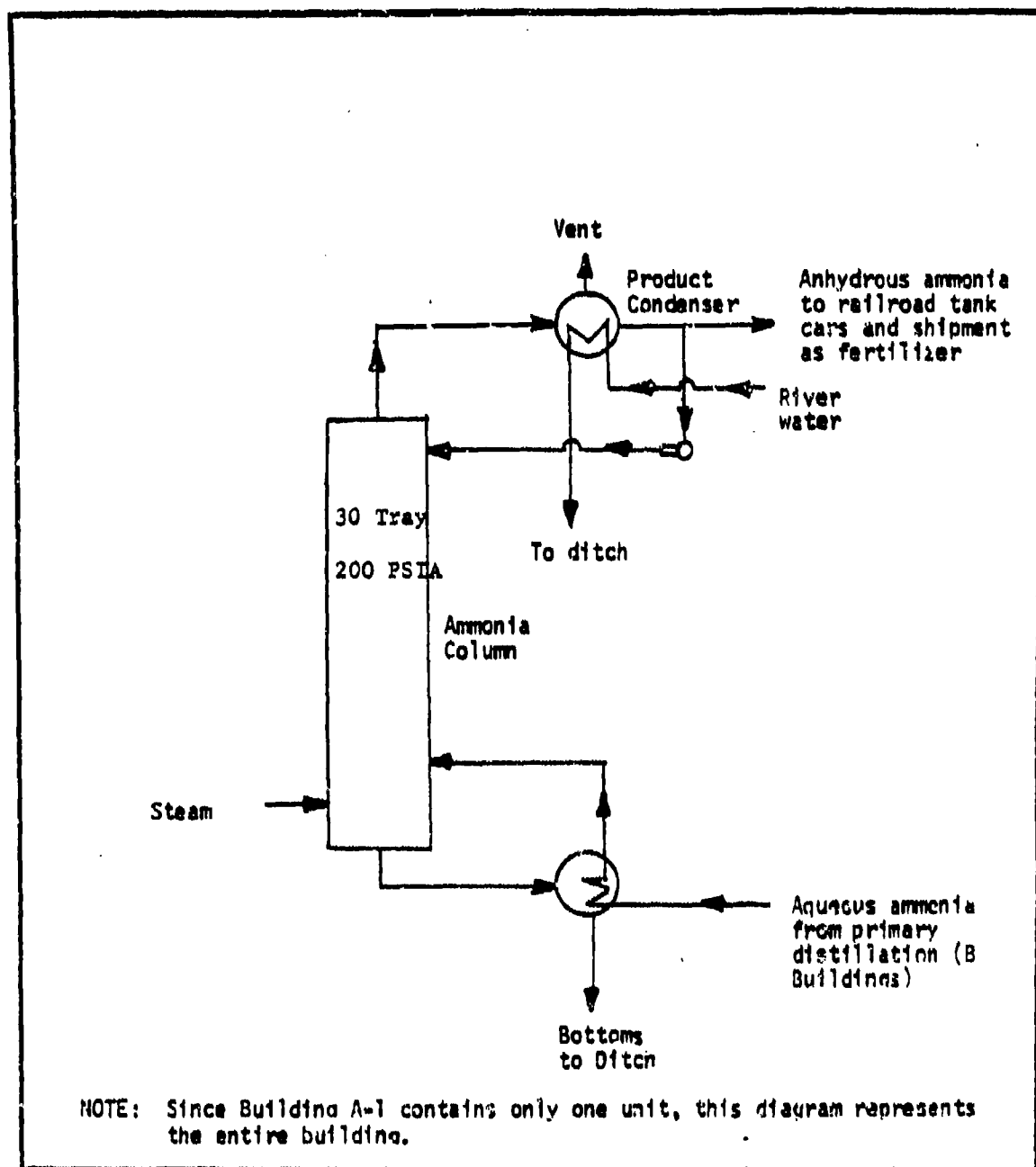


Figure I-11. Ammonia Distillation in Building A-1 (USAEHA, 1971).

tures and pressures, formaldehyde and ammonia react to form hexamine (Campbell, 1976). The bottom products from the A-1 Building column contain hexamine (~ 5,000 ppm), ammonia (~ 5,500 ppm), formaldehyde (~ 180 ppm), methylamine (~ 3,500 ppm), dimethylamine (~ 2,200 ppm), trimethylamine (~ 180 ppm) and copper (12.5 ppm) (Adams and Whiting, 1976). This waste stream is discharged into Arnott Branch. At current operation levels, the A-1 Building still is operated one week every four months. Discharges from the still are ~ 21,000 gallons per day (USA-EHA, 1971). This waste flow is based on a feed rate of 15 gallons per minute.

3. Characterization of Effluents from the Manufacture of RDX/HMX

The surface runoff and cooling water from the Area B production facilities are discharged into ditches which lead directly to the Holston River. Process effluents from the RDX/HMX manufacture itself are discharged through catch basins into industrial sewer lines which empty directly into the Holston River or Arnott Branch. Holston Defense Corporation routinely monitors the industrial sewer effluents as well as the Area B water inlet and two stations on the Holston River downstream from Area B.

The locations of the sampling stations for Holston AAP Area B industrial effluents are shown in Figure Y-2.

- Station B01A is located at the Area B pumping station and monitors the quality of the inlet water.
- Station B02B is located at Manhole No. 300 where the underground industrial sewer line emerges into an open ditch. This line carries process effluents from Buildings C through N on lines 6 and 7. The flow rate at this station was estimated to be between 0.5 and 1.5 MGD in 1976 and 1977 (Hash, 1978).
- Station B02A is located directly on the Holston River at the end of industrial sewer line No. 302. This line serves Buildings G through N on lines 1 through 5. Flow rates from sewer line No. 302 were estimated to be between 0.5 and 1.0 MGD in 1976 and 1977 (Hash, 1978).
- Station B03B is located on Arnott Branch. The industrial effluents from the C and D Buildings of lines 1 through 5, the B Buildings, the A-1 ammonia recovery still and the nitric acid facilities flow directly into Arnott Branch. The flow at the B03B station is ~ 20-22 MGD (Hash, 1978). This number represents a total combined flow rate of the process effluents and Arnott Branch. The upstream Branch flow is 12 MGD. Process effluent flow rate averages between 8 and 10 MGD.
- Station B01B is at Igloo Bridge on the Holston River

down stream from the entry of Arnott Branch.

- Station BO1C is at Churchill Bridge, downstream from Holston AAP Area B.

The flow of the Holston River varies considerably within a twenty-four hour period due to the intermittent releases from Ft. Patrick Henry Dam (Sullivan *et al.*, 1977). This intermittent variation in river flow conditions influences the ability of the river to dilute HAAP Area B wastes. The dilution factor has been shown to vary by 12 over a two hour period (Sullivan *et al.*, 1977). In addition to the flow variation, dye tracer studies have shown that the mixing of the North and South Forks is not complete until mile 137 (~ 1 mile down stream from Arnott Branch). Thus the North and South Forks behave as two contiguous streams occupying the same river bed from the point of convergence to mile 137 (Sullivan *et al.*, 1977). The result is widely differing water qualities on the North and South banks of the River and relatively little dilution of HAAP Area B wastes for at least one mile downstream.

Many studies have been conducted to determine the various levels of discharges from Holston AAP and their effects on the Holston River (Sullivan *et al.*, 1977; Bender *et al.*, 1977; Patterson *et al.*, 1976b; Huff *et al.*, 1975; USAEHA, 1972; USAEHA, 1971; Heidelberger, 1971). The reader is referred to the original documents for earlier sampling data. Analyses for 1976 and 1977 are presented in Tables I-5 and I-6. Inspection of these tables shows the following:

1. Of the compounds of interest to this study, only cyclohexanone is monitored on a regular basis.
2. The water quality of the effluent streams varies widely throughout the year (Table I-5) and even during biweekly sampling (Table I-6).
3. As would be expected, cyclohexanone appears in streams BO2A and BO2B which contain the effluents from the G Recrystallization Building and the H Dewatering Building. RDX, HMX and TNT were also found in the largest quantities in these two streams.
4. Nitrates are predominant in stream BO3B.

Estimates of the amount of explosives and related compounds discharged from HAAP at production levels of 275 tons/day of Composition B have been made by Patterson *et al.* (1976b). These estimated discharges are:

Table 1-5. Water Quality Data Summary (1976-1977) - Area B Holston AAP (HDC, 1978).

1976 Summary	Sampling Point	DOB	COB	IC	OC	RHE	MSE	TST	TAX	SEX	pH	Nitrate mg/L	Organic N	Dissolved Solids	Acetone	Cyclo- hexanone
Mean	DOA	3	20	19	11	0	0	0	-	-	7.4	7.4	0.1	162	0	0
S.D.		2.6	3.6	2.7	4.8	0	0	0	-	-	0.17	3.64	0.23	34.1	0	0
High		9	26	27	25	0	0	0	-	-	7.7	16.0	1.0	106	0	0
Low		1	16	16	5	0	0	0	-	-	7.1	4.4	0.0	104	0	0
No. of observations		13	5	16	16	5	5	5	0	0	17	16	17	4	5	5
Mean	DOA	100	167	27	67	7.6	6.6	2.4	-	-	6.7	6.3	0.4	142	10	10
S.D.		72.4	115	4.6	47.5	7.43	11.99	2.13	-	-	0.43	3.32	0.06	12.7	24.0	12.76
High		259	295	25	197	32.9	59.3	8.6	-	-	7.6	16.0	2.0	180	96	44
Low		4	23	6	16	0	0	0	-	-	5.4	2.5	0	124	0	0
No. of observations		38	5	29	29	25	25	25	5	5	35	29	35	4	26	26
Mean	DOA	154	279	17	83	5.5	2.6	0.3	-	-	6.7	6.9	0.2	144	41	4
S.D.		156.91	282.2	5.1	186.7	10.55	2.44	1.13	-	-	0.7	2.18	0.52	16.0	85.6	12.96
High		637	798	25	333	42.2	15.9	4.2	-	-	7.0	18.1	1.8	182	397	55
Low		0	28	5	16	0	0	0	-	-	5.6	1.9	0	113	0	0
No. of observations		11	5	29	29	25	25	25	0	0	32	29	35	4	26	26
Mean	DOA	2	23	21	14	0	0	0	-	-	7.5	10.3	0.3	142	2	0
S.D.		2.2	3.7	1.6	6.5	0.09	0.09	0	-	-	0.56	7.28	0.48	36.1	7.7	0
High		9	29	18	32	0.3	0.4	0	-	-	8.0	35.9	2.7	175	39	0
Low		1	1	1	5	0	0	0	-	-	5.9	5.0	0	210	0	0
No. of observations		33	5	25	28	25	25	25	0	0	35	29	35	4	26	26
Mean	DOA	2	18	19	8	0.0	3.2	0	-	-	7.4	7.0	0	167	1	0
S.D.		1.7	5.1	2.5	2.8	0.19	0.19	0	-	-	0.15	4.11	0	51.1	2.3	0
High		7	26	32	19	0.1	0.5	0	-	-	7.9	14.5	0	230	7	0
Low		1	14	17	3	0	0	0	-	-	7.1	4.0	0	120	0	0
No. of observations		15	5	16	16	0	0	0	0	0	17	17	17	5	9	9

1977 Summary	Sampling Point	DOB	COB	IC	OC	RHE	MSE	TST	TAX	SEX	pH	Nitrate mg/L	Organic N	Dissolved Solids	Acetone	Cyclo- hexanone
Mean	DOA	2	14	21	10	0	0	0	-	-	7.6	6.5	0.4	171	0	0
S.D.		2.4	5.7	3.0	6.2	0	0	0	-	-	0.19	2.44	1.61	34.0	0	0
High		6	27	27	25	0	0	0	-	-	7.9	12.5	5.0	229	0	0
Low		1	9	19	3	0	0	0	-	-	7.4	3.0	0	124	0	0
No. of observations		11	11	16	10	5	5	5	0	0	11	11	10	11	5	5
Mean	DOA	43	103	21	28	3.0	2.9	0.5	-	-	7.2	5.7	0.1	178	4	0
S.D.		44.4	62.6	1.9	17.5	2.55	2.51	0.69	-	-	0.4	2.22	0.6	36.4	5.5	6.13
High		179	219	26	34	7.6	8.4	2.1	-	-	7.6	10.5	0.7	231	32	15
Low		0	19	17	10	0.6	0.9	0	-	-	6.9	2.7	0	105	0	0
No. of observations		8	11	16	10	5	5	5	0	0	11	11	11	13	9	9
Mean	DOA	91	140	20	27	1.3	1.4	0.1	-	-	7.3	6.3	0.1	179	5	5
S.D.		126.4	137.2	3.3	21.5	1.43	1.3	0.16	-	-	0.28	2.31	0.16	34.1	6.6	5.6
High		306	418	35	60	6.0	4.1	0.4	-	-	7.7	11.7	0.4	267	20	15
Low		3	21	15	10	0.1	0	0	-	-	6.9	3.9	0	161	0	0
No. of observations		9	11	16	10	5	5	5	0	0	11	11	11	11	9	9
Mean	DOA	3	19	22	9	0	0	0	-	-	7.6	17.7	0.3	197	0	0
S.D.		1.5	6.6	3.6	3.7	0.9	0	0	-	-	0.22	7.56	0.5	32.3	0	0
High		7	30	29	15	0.3	0.1	0	-	-	8.0	31.2	1.6	263	0	0
Low		2	9	19	2	0	0	0	-	-	7.1	6.5	0	150	0	0
No. of observations		11	11	16	10	5	5	5	0	0	11	11	10	13	9	9
Mean	DOA	2	14	22	13	0	0	0	-	-	7.6	7.0	0.1	174	-	-
S.D.		1.9	6.6	4.2	12.0	0	0	0	-	-	0.09	2.65	0.22	32.2	1	0
High		8	31	31	45	0	0	0	-	-	7.0	13.2	0.6	223	1.6	0
Low		1	8	17	2	0	0	0	-	-	7.5	4.4	0	164	5	0
No. of observations		11	11	16	10	5	5	5	0	0	11	11	10	11	9	9
Mean	DOA	1	14	23	10	-	-	-	-	-	7.6	6.8	0.1	180	0	0
S.D.		0.5	4.0	3.9	5.3	-	-	-	-	-	0.14	3.31	0.26	22.7	0	0
High		2	19	33	16	-	-	-	-	-	7.9	12.6	0.8	226	0	0
Low		1	9	18	3	-	-	-	-	-	7.5	2.0	0	159	0	0
No. of observations		6	6	6	6	0	0	0	0	0	6	6	6	6	6	6

Table I-6. Water Quality Data for 1977 - Area B Holston AAP (UDC, 1973).

Date month/year	Sampling Point	WQ	DO	IC	OC	AK	ME	WT	LM	ph	Mitrazo mg/L	Organic N	Dissolved Solids	Acetone	Cyber- bromine
3/77	B01A	2	21	-	-	0	0.9	0.4	-	7.7	7.4	0	124	0	0
	B01B	13	16	-	-	3.2	1.1	0.4	-	7.4	6.4	0	145	10	15
	B01C	200	4	-	-	1.6	0	0.4	-	7.9	0.1	0	150	20	5
	B01D	4	26	-	-	0	0	0	-	7.4	31.5	0	150	0	0
	B01E	3	30	-	-	0	0	0	-	7.4	5.7	0	148	5	0
4/77	B01A	3	16	21	11	0	0	0	-	7.5	6.4	0	130	0	0
	B01B	8	19	20	10	0.6	2.1	0	-	7.5	7.5	0	135	0	5
	B01C	93	146	20	26	0.6	0	0	-	6.9	0.0	0	161	5	13
	B01D	5	15	19	15	0	0	0	-	7.4	20.9	0	176	0	0
	B01E	3	16	20	12	0	0	0	-	7.4	6.4	0	137	0	0
6/77	B01A	6	19	24	6	-	-	-	-	7.5	6.3	0	207	-	-
	B01B	-	144	21	25	-	-	-	-	7.6	6.8	0	376	-	-
	B01C	-	193	20	41	-	-	-	-	7.4	5.3	0	155	-	-
	B01D	8	15	19	10	-	-	-	-	7.4	16.4	0	170	-	-
	B01E	8	31	22	10	-	-	-	-	7.5	6.4	0	216	-	-
8/77	B01A	3	10	21	3	0	0	0	-	7.7	6.2	0	130	0	0
	B01B	-	155	26	26	2.5	2.6	0.5	-	7.0	2.7	0.1	155	5	10
	B01C	4	22	20	5	4.0	1.2	0.1	-	7.6	6.1	0	151	0	0
	B01D	3	9	20	2	0	0	0	-	7.7	11.4	0.2	150	0	0
	B01E	3	9	20	2	0	0	0	-	7.7	5.5	0	146	0	0
10/77	B01A	2	11	21	10	0	0	0	-	7.4	6.1	0	144	0	0
	B01B	27	113	16	24	7.4	4.4	2.1	-	7.1	6.6	0	310	5	15
	B01C	3	45	17	34	0.2	2.7	0	-	7.7	0.1	0.1	312	10	0
	B01D	3	22	20	10	0	0	0	-	7.7	12.5	0	316	0	0
	B01E	2	13	20	9	0	0.1	0	-	7.7	0.3	0	140	0	0
12/77	B01A	3	17	18	6	0	0	0	-	7.4	3.8	0.7	142	0	0
	B01B	25	67	20	21	3.7	1.0	0.1	-	7.2	4.2	0.2	214	0	0
	B01C	244	344	15	0	0.1	0.9	0	-	7.1	3.9	0.3	247	5	10
	B01D	4	15	22	0	0	0	0	-	6.0	0.5	1.4	213	0	0
	B01E	2	4	17	4	0	0	0	-	7.6	6.4	0.4	172	0	0
1/77	B01A	2	10	16	3	-	-	-	-	7.7	4.4	0.2	170	0	0
	B01B	5	19	19	9	0	0	0	-	7.4	0.2	3.2	229	0	0
	B01C	7	54	17	10	0.6	1.1	0	-	7.5	6.2	0.3	185	0	0
	B01D	7	37	17	15	0.6	1.1	0	-	7.3	5.0	0.3	175	0	0
	B01E	3	26	25	12	0	0	0	-	7.4	11.9	0.6	213	0	0
3/77	B01A	2	4	31	37	0	0	0	-	7.4	0.5	0	223	0	0
	B01B	1	15	33	32	-	-	-	-	7.9	0.5	0	226	0	0
	B01C	2	12	26	16	0	0	0	-	7.6	6.4	0.5	177	0	0
	B01D	80	150	26	34	6.3	4.2	0.9	-	6.5	3.0	0.7	180	12	15
	B01E	4	42	25	10	3.0	1.4	0	-	7.5	7.0	0.4	173	5	4
5/77	B01A	2	12	27	4	0	0	0	-	7.1	15.4	0.4	191	0	0
	B01B	2	12	27	4	0	0	0	-	7.5	3.5	0.6	181	0	0
	B01C	2	15	27	4	0	0	0	-	7.5	3.9	0.6	175	0	0
	B01D	2	13	27	15	0	0	0	-	7.4	6.9	0	172	0	0
	B01E	31	65	25	34	0.6	1.0	0.1	-	7.2	5.1	0	184	0	0
7/77	B01A	3	21	25	16	0.1	0	0.1	-	7.7	5.6	0	161	0	0
	B01B	2	17	25	13	0	0	0	-	7.5	17.4	0	180	0	0
	B01C	1	9	25	13	0	0	0	-	7.6	6.0	0	171	0	0
	B01D	1	9	25	16	-	-	-	-	7.6	6.8	0	176	0	0
	B01E	1	9	19	0	0	0	0	-	7.6	7.5	0.1	156	0	0
9/77	B01A	139	219	20	21	2.6	4.2	0	-	7.2	5.0	0	161	5	0
	B01B	135	219	19	44	2.0	0	0	-	7.3	6.0	0	171	0	0
	B01C	7	30	20	5	0	0	0	-	7.6	10.3	0.5	190	0	0
	B01D	1	13	10	10	0	0.1	0	-	7.6	7.5	0.3	154	0	0
	B01E	1	18	14	0	-	-	-	-	7.6	7.4	0	150	0	0
11/77	B01A	2	23	20	25	-	-	-	-	7.4	12.5	0	212	0	0
	B01B	-	20	24	23	-	-	-	-	7.2	10.5	0	231	0	0
	B01C	-	71	22	10	-	-	-	-	7.1	11.7	0	232	0	0
	B01D	4	22	20	9	-	-	-	-	7.2	11.2	0.9	242	0	0
	B01E	2	16	22	45	-	-	-	-	7.5	12.4	0	234	0	0
12/77	B01A	2	19	20	17	-	-	-	-	7.5	15.6	0	223	0	0

RDX	- 124 lb/day	0.451 lb/ton of product
HMX	- 45.2 lb/day	0.164 lb/ton of product
TNT	- 81.8 lb/day	0.297 lb/ton of product
Hexamine	- 30 lb/day	0.109 lb/ton of product
Solvents	- 1230 lb/day	4.47 lb/ton of product

From these numbers, discharges at full mobilization (~ 750 tons of product/day) can be estimated as follows:

RDX	- ~ 340 lb/day
HMX	- ~ 123 lb/day
TNT	- ~ 225 lb/day
Hexamine	- ~ 75 lb/day
Solvents	- ~ 3352 lb/day

These numbers represent minimum discharge levels. Other estimates of discharges at full mobilization are significantly higher. For example, Epstein *et al.* (1976) estimated the TNT discharge from Holston at full mobilization to be 650 lb/day.

4. Future Effluent Treatment Plans

Currently all Holston AAP Area B wastes enter the Holston River without any pretreatment. In 1973, Clark, Dietz and Associates-Engineers, Inc. was awarded a contract to design a wastewater treatment facility for Area B process effluents. During this investigation, Area B wastes were collected for evaluation of biological treatability by Purdue University. These studies showed that activated sludge systems were not suited for treatment of Area B wastes due to formation of filamentous growth. Studies on the ammonia recovery bottoms indicated that this stream could not be treated biologically or chemically. Wet-oxidation was recommended for treatment of this stream. For treatment of general Area B wastewaters, Clark-Dietz (Hash *et al.*, 1977) recommended a fixed-film denitrification (submerged anaerobic filters) and aerobic fixed-filter reactors (trickling filters). However, sufficient information was not obtained from these studies for final design.

In 1974, Holston Defense Corporation was awarded a contract for pilot scale verification of the system recommended by Clark-Dietz. This pilot unit was also to evaluate the effect of Area A wastes on the treatment process. As a result of this pilot study, a three stage biological treatment system was recommended to treat combined Area A and B wastes with the exception of the ammonia recovery bottoms (Hash *et al.*, 1977). This facility would consist of

- anaerobic tower
- trickling filter
- activated sludge

The best performance in the pilot study was observed with a trickling

filter and activated sludge systems in series while operating at a 6 hour aeration time (Hash *et al.*, 1977).

In this pilot study, RDX, HMX and TNT in the wastes were not toxic to the microorganisms. However, complete removal of these compounds would not be expected in the treatment facility. Tertiary treatment will be necessary to comply with 1983 EPA standards.

Plans are currently underway to build the biological treatment facility at Holston AAP. The site of this facility is shown in Figure 1-2. A pipeline which will take the process effluents to the treatment facility is already under construction. This biotreatment facility will be capable of handling the 12.5 MGD process effluents which would result during full mobilization (Hash *et al.*, 1977).

Tertiary treatment processes for removal of RDX, HMX and TNT were investigated by Jackson *et al.* (1976). Processes which were evaluated include anaerobic biodegradation, chemical oxidation, coagulation, reverse osmosis, polymeric adsorption and carbon adsorption. Anaerobic biodegradation, chemical oxidation and activated carbon adsorption removed 100% of the RDX and HMX from solution.

Due to the toxicity of the Ammonia Recovery bottoms in the original study (Clark-Dietz, 1974), several studies have been conducted to determine the best method of treating this waste stream.

1. Wet oxidation was found to be an effective treatment method, however, the cost is prohibitive (Hash *et al.*, 1977).

2. A distillation method for concentration of hexamine to 15 to 30 wt % was proposed by Campbell (1976). The results are based on theory and proposed methodology has not been piloted.

3. Studies on biological nitrification/denitrification of the A-1 effluent showed that formaldehyde (<180 ppm) and hexamine (<500 ppm) would not inhibit nitrification/denitrification. However, the methylamines and copper were toxic to the microorganisms (Adams and Whiting, 1976). The authors recommended addition of ethylenediaminetetraacetic acid (EDTA) to eliminate the copper toxicity and pretreatment with aerobic bacteria to eliminate the methylamine toxicity. A 1/10 dilution was also recommended before this effluent enters the general biotreatment facility.

In general, it appears that a single biotreatment facility will not lead to water of sufficient quality to meet the 1983 EPA standards. RDX, HMX, TNT, SEX, TAX, hexamine and the methylamines appear to be the major problems to meeting the 1983 EPA standards.

B. TNT Manufacture

1,3-dinitrobenzene and 1,3,5-trinitrobenzene are minor impurities in the TNT product. They are also found in and resulting from the effluents from the TNT and DNT manufacture, blending and loading operations. TNT manufacturing facilities are located at

- Radford AAP (RAAP), Radford, Virginia
- Newport AAP (NAAP), Newport, Virginia
- Joliet AAP (JAAP), Joliet, Illinois
- Volunteer AAP (VAAP), Chattanooga, Tennessee.

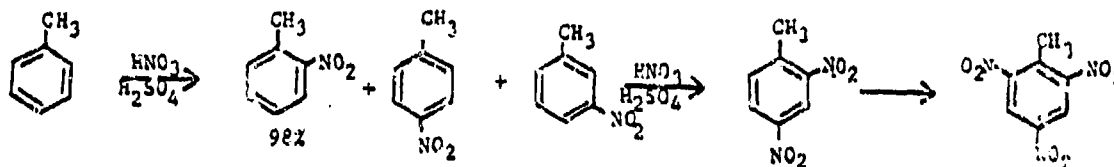
TNT is blended with RDX or HMX and other ingredients at Holston AAP in Kingsport, Tennessee. TNT and TNT blends are loaded at the following LAP plants:

- Cornhusker AAP (CAAP), Grand Island, Nebraska (Inactive)
- Iowa AAP (IAAP), Middletown, Iowa
- Joliet AAP (JAAP), Joliet, Illinois (Inactive)
- Kansas AAP (KAAP), Parsons, Kansas
- Lone Star AAP (LSAAP), Texarkana, Texas
- Louisiana AAP (LAAP), Shreveport, Louisiana
- Milan AAP (MAAP), Milan, Tennessee

1. Manufacturing Facilities

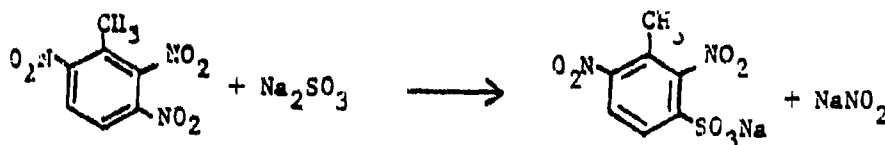
TNT is manufactured by either a batch or the CIL continuous process. The batch process is being phased out and the batch lines replaced with continuous lines. Each TNT line is capable of producing 100,000 lb of TNT per day. Newport AAP has four continuous lines; Joliet has three batch and six CIL continuous lines; Volunteer has six batch and six CIL continuous lines; and Radford is installing 2 continuous lines to replace those damaged in a May 1974 explosion. Currently, no TNT is being produced in the United States. The most recent production was at Volunteer AAP which had one line in operation until March 1977. However, upon completion of the two lines at Radford AAP, production of TNT is expected to resume at Radford AAP (Epstein *et al.*, 1976).

TNT is manufactured by the successive nitration of toluene with oleum.



The two processes used in this manufacture are shown schematically in Figures I-12 and I-13. Since the batch process is being phased out, it will not be described in detail in this report.

In the CIL continuous process, the nitration is carried out in six nitrator-separators. The process utilizes countercurrent flow of toluene and the nitrating acids. The crude TNT oil is slurried with water and the excess acid neutralized with sodium carbonate. The wash water, called "yellow water", contains acids and some nitrogen containing compounds. Purification of the crude TNT is accomplished by the Sellite process. In the Sellite purification, the TNT is washed with sodium sulfite. During this wash, TNT isomers having a nitro group in the meta position (i.e. δ -TNT, γ -TNT or 3-TNT) react to form the sodium salt of the 3-sulfonic acid derivatives and sodium nitrite.



With tetranitromethane, sodium sulfite reacts to form sodium trinitromethane sulfonate:



The salts formed are water soluble and are washed from the TNT with water. The resulting water is called "red water." Sodium sulfite does not react with DNT, trinitrobenzoic acid or 1,3-dinitrobenzene. Thus only minor amounts of these compounds are removed by the wash and they are impurities in the TNT product.

Following the Selliting and water washing, the purified TNT is dried in hot air. Once dried, it is solidified and flaked on a water-cooled drum.

The CIL continuous process differs from the old batch process in several ways

- water is used in place of sodium carbonate for initial acids removal
- the sellite solution is prepared directly from dry sodium sulfite instead of by a SO_2 -carbonate reaction
- less waste water is generated containing lower amounts of nitrogen containing compounds

A comparison of the wastewater generated by the batch and CIL process is presented in Table I-7 (Patterson *et al.*, 1976b).

2. Process Effluent Streams

As shown in Figures I-12 and I-13, there are three major waste streams from TNT manufacture.

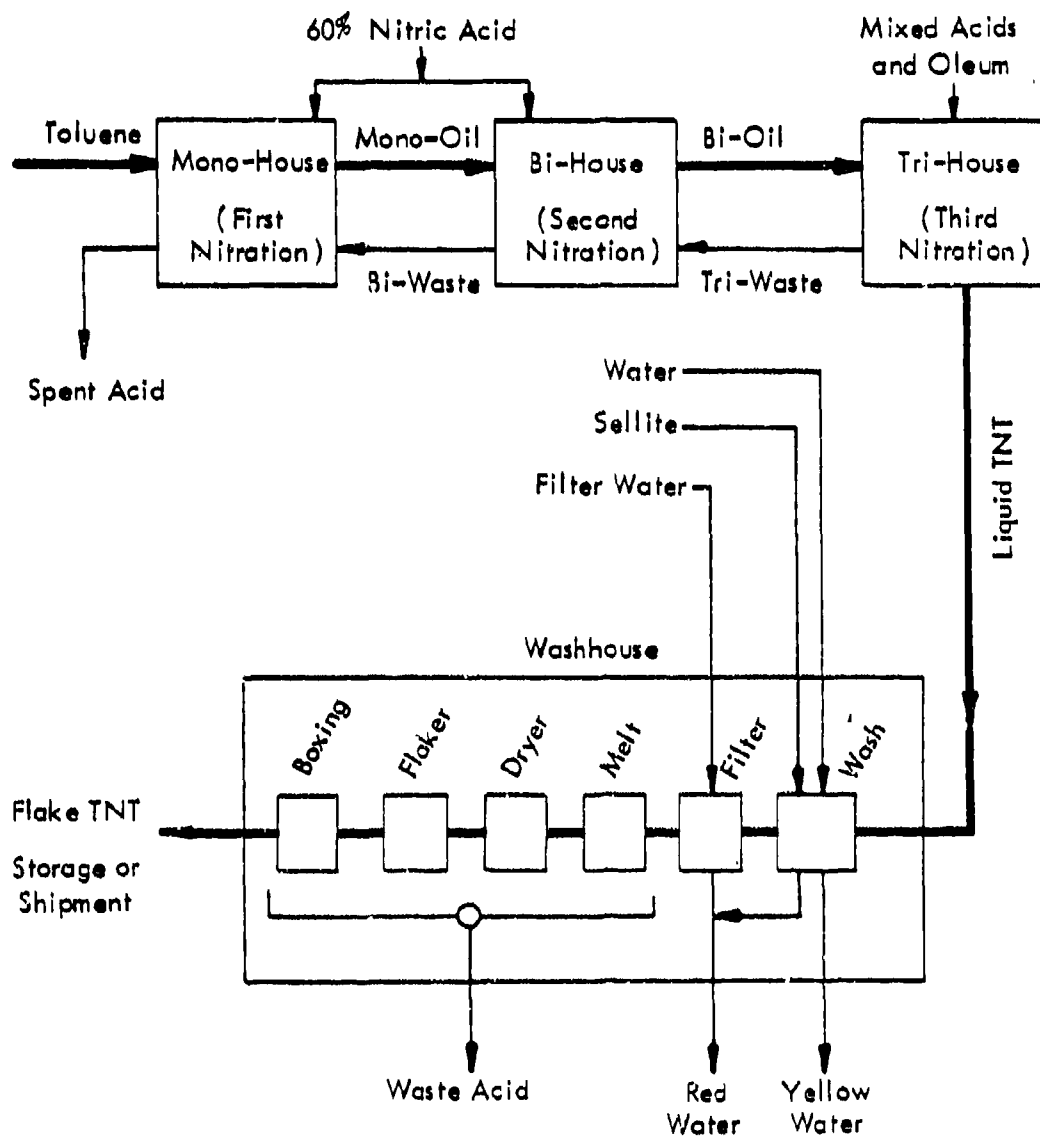


Figure I-12. Manufacture of TNT by the Batch Process
(Patterson *et al.*, 1976a).

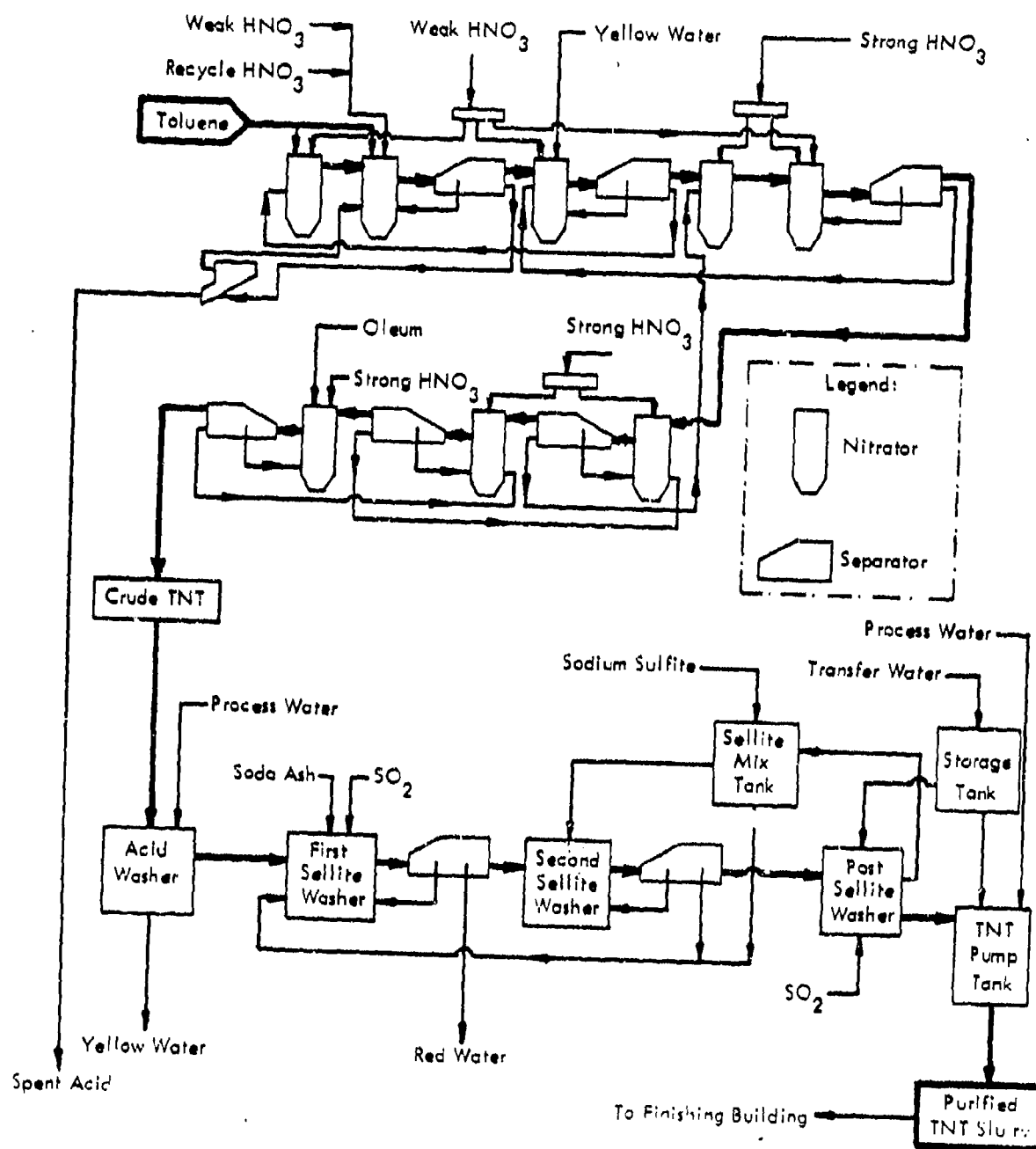


Figure I-13. Manufacture of TNT by the CIL Continuous Process
(Patterson et al., 1976a)

Table I-7. Comparison of the Overall Discharges Resulting from the Production of TNT by the Batch and CIL Continuous Process.

Chemical Parameter	RAAP*		JAAP**	
	Discharge (lb/day)	Discharge (lb/ton of product)	Discharge (lb/day)	Discharge (lb/ton of product)
Acidity/CaCO ₃	2,700	18.6	1,290	4.27
Alkalinity/CaCO ₃	2,530	17.4	12,200	40.4
Total Solids	10,500	72.4	83,274	275
Suspended Solids	1,510	10.4	1,240	4.10
Dissolved Solids	8,980	61.9	80,700	267
Volatile Solids			35,600	117
COD	620	4.27		
TKN	30.9	.213	511	1.69
NO ₂ + NO ₃ /N	255	1.76		
NO ₃ /N			1,270	4.20
SO ₄	5,230	36.1	39,600	131
TNT	167 (63.5 mg/l)	1.15	60 (6.25 mg/l)	.199
TOC			11,400	37.7
Sulfides			476	1.58
Water Volume	2.63 mgd		9.60 mgd	
Gal per ton of Final Product	18,100		31,800	

*145 ton/day TNT produced; **302 ton/day TNT produced

- spent acid
- yellow water
- Red Water

None of these streams are discharged directly. The spent acids are sent to the acid recovery unit. The yellow water is returned to the second nitration or combined with the Red Water. Red Water is disposed of by evaporation-concentration at Volunteer and Joliet AAP. Newport concentrates the waste and incinerates it. Radford sells the Red Water to paper mills.

Pink Water arises from the nitration fume scrubber discharges; Red Water distillates; and finishing building hood scrubber and washdown effluents. Some Pink Water could also be in the spent acid recovery wastes (Patterson *et al.*, 1976b). The Pink Water streams are discharged from the AAP; thus, the Pink Water represents the major streams in which 1,3-dinitrobenzene and 1,3,5-trinitrobenzene or its precursor 1,3,5-trinitrobenzoic acid can enter the environment from TNT manufacture.

C. Explosives Blending and Loading Operations

1. Explosives Blending

RDX, HMX and TNT are blended into various compositions at HAAP. Process water from the incorporation buildings is flowed through catch basins and then directly into the Holston River. This incorporation step involves mixing of wet RDX or HMX with other ingredients such as molten TNT. The excess water is decanted into the catch basins and ultimately to the Holston River. Thus, the incorporation step is a source of pollution not only from the major explosives but also from the more soluble minor impurities such as SEX, TAX, 1,3-dinitrobenzene and 1,3,5-trinitrobenzene in these explosives.

2. Explosives Loading, Assembly and Pack

Explosives containing RDX, HMX and/or TNT are loaded at seven LAP plants

- Cornhusker AAP (CAAP)
- Ecwa AAP (IAAP)
- Joliet AAP (JAAP)
- Kansas AAP (KAAP)
- Lone Star AAP (LSAAP)
- Louisiana AAP (LAAP)
- Milan AAP (MAAP)

These plants all generate Pink Water. The mission and the Pink Water disposal at each of these plants is discussed briefly in the following sections.

a. Cornhusker AAP

Cornhusker AAP, located in Grand Island, Nebraska, is currently inactive. The primary mission of this plant is loading of heavy munitions including

- eight-inch shells loaded with pure TNT
- 500-, 750-, 1000-lb bomb loaded with tritonal (80% TNT, 20% flaked aluminum)

The waste water volume from each load line is estimated between 6,300 gallons and 28,800 gallons per day. This water is disposed of by percolation and evaporation in tanks and basin above each load line. These basins have no outfalls (Patterson et al., 1976b).

b. Kansas AAP

Kansas AAP, located in Parsons, Kansas, melt-pours RDX-TNT mixtures into 81 mm, 105 mm and CBU shells. The wastewaters from these operations are trucked to evaporation ponds.

c. Lone Star AAP

Pink water is generated in four areas at LSAAP near Texarkana, Texas. The effluent from the Area O melt-pour line is discharged directly to the Red Water Lakes (Patterson et al., 1976b). The pink water from melt-pour Areas C, E and G are passed through anthracite coal to remove suspended solids. This water is then reused. When the TNT concentrations become excessive, the water is trucked to holding ponds. Carbon adsorption treatment facilities for pink water abatement are currently under construction at LSAAP.

d. Louisiana AAP

Louisiana AAP is located in Shreveport, Louisiana. Contaminated water (~ 138,000 gpd containing 80 mg/l TNT at full capacity) from shell loading is trucked to leaching ponds.

e. Milan AAP

Milan AAP, located in Milan, Tennessee, loads a variety of products including 40, 60, 81, 90, 105, 106 mm shells, mines and grenades. The wastewater from these operations are discharged into a drainage canal which flows to surface water. Patterson et al. (1976b) estimated that the current overall daily discharge of TNT and RDX is 3.5 lb/day and 2.7 lb/day, respectively.

f. Iowa and Joliet AAP

Iowa AAP, located in Middletown, Iowa, loads a variety of shells. Joliet AAP, Joliet, Illinois, loads medium caliber ammunition in

addition to production of TNT. The LAP wasdown and scrubber effluents from these plants are currently being treated by carbon adsorption. The waters are collected in catch basins, filtered through diatomaceous earth then through two granulated charcoal columns. The effluent from the columns is discharged to surface drainage. A schematic of the carbon adsorption water treatment facility is shown in Figure I-14. Performance figures for the carbon treatment system at JAAP are presented in Table I-8. Although the performance of the system has been good, many technical and cost problems remain to be resolved. These problems include

- clogging of the diatomaceous earth filter by wax
- effect of pH and minor chemicals on the column efficiency
- effective maintenance schedule
- air pollution from burning of the used carbon
- efficient carbon regeneration system.

3. Future Pink Water Treatment

Although carbon adsorption is currently being used for pink water abatement, the ability of carbon to economically treat pink water at full mobilization is of concern. Other destruction methodologies which are being investigated include (Patterson et al., 1976c; Tatyrek, 1976)

- ozonolysis
- solvent extraction using toluene
- reverse osmosis
- absorption on fly ash
- polymeric ion exchange resins
- biotreatment
- foam separation
- wet oxidation
- incineration
- catalytic wet oxidation
- composting and soil disposal

Most of these treatment methodologies are not yet sufficiently developed to determine their treatment and cost effectiveness.

D. Disposal of Solid Explosives Wastes

1. Wastes from Explosives Manufacturing

Solid RDX, HMX and TNT from the manufacturing and blending operations at HAAP include off-spec material and solids removed from the catch basins. TNT solid wastes are also generated at RAAP, JAAP, NAAP and VAAP when these plants are in operation. Currently all the solid wastes from the manufacturing process are burned in open burning grounds. This burning leads both to air pollution problems and soil contamination problems.

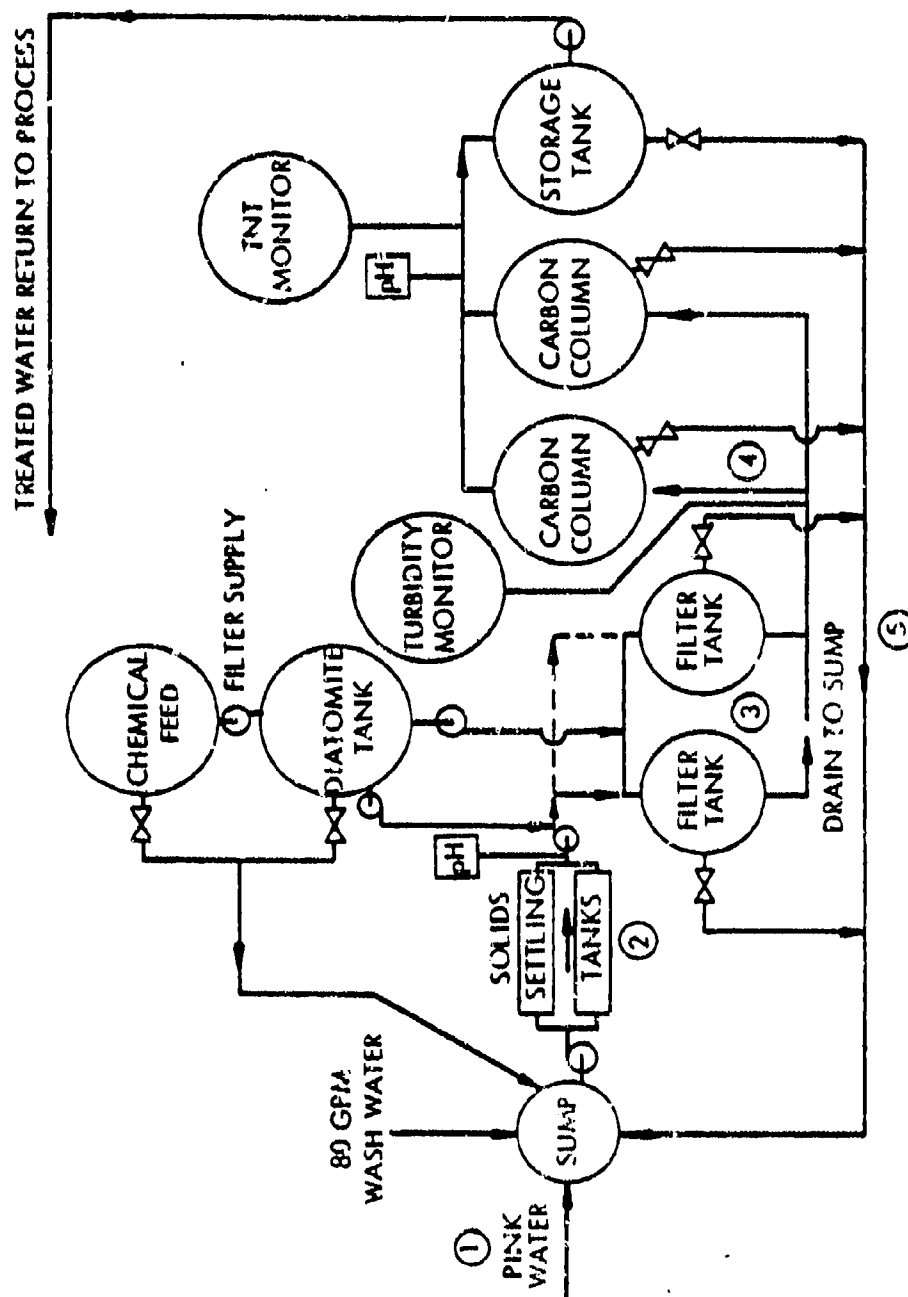


Figure I-14. Schematic of Carbon Adsorption Treatment of Pink Water at LAP Plants (Patterson *et al.*, 1976c).

Table 1-8. Performance of LAP Wastewater Treatment System at Joliet AAP (Patterson *et al.*, 1976c).

Parameter	LAP Influent		Effluent From:								Average Percent Change
	Range	Average	Dist. Earth Filter		1st Carbon Column		2nd Carbon Column				
			Range	Average	Range	Average	Range	Average			
pH	6.8-8.4	7.9	7.6-8.6	7.9	7.6-8.2	7.8	6.7-8.0	7.7	-		
Total Solids	903-1790	1401.5	959-1796	1418.5	794-1791	1138.3	762-1497	1069.8	23.7		
Suspended Solids	220-336	138.5	26.0-271.0	108.6	0.0-40.0	8.4	0.0-7.0	1.2	99.1		
TOC	93-188.4	121.1	100.0-162.0	121.1	5.9-64.0	24.3	7.8-20.9	12.1	90.0		
Kjeldahl-N	10.3-25.4	17.0	8.9-23.0	15.3	4.4-8.6	7.2	4.0-4.9	4.6	72.9		
TNT	156.2-235.0	178.2	143.5-213.0	175.7	0.0-111.2	14.7	0.0-25.0	3.7	97.9		
RDX	87.5-180.0	145.2	87.5-185.0	148.9	0.0-77.5	30.1	0.0-46.4	19.5	86.6		
Color	-	-	-	-	5.0-20.0	10.0	0.0-20.0	8.0	-		

*All units except pH and color in mg/l. Color in PTU.

In the future, each plant will have contaminated waste incinerators. Air curtain incinerators are scheduled for installation at HAAP. An air curtain incinerator is already in operation at RAAP for burning contaminated wastes. A rotary kiln explosives waste incinerator was installed at RAAP in 1977. However, it does not meet performance specifications and will have to be modified. This incinerator should be operational in late 1978 or early 1979.

2. Wastes from Explosives Loading Operations

Solid wastes from explosives loading operations include spilled explosives from the press loading operations and filtered solids, contaminated diatomaceous earth and carbon from the melt-pour loading operations. These solid wastes are currently burned in open burning grounds. Thus, they present a source of air and soil pollution. Incinerators for destroying contaminated solid wastes are now being or will be installed at the various explosives LAP plants. In addition, a carbon regeneration system is currently being piloted at Iowa AAP. This system is a rotary calciner (Buckley *et al.*, 1977). The carbon is regenerated in three zones

- zone 1 - 110°C to dry the carbon
- zone 2 - 300°C to decompose the TNT
- zone 3 - 1500°C CO₂ and steam to regenerate the carbon

The process gives good carbon recovery and adsorptive capacities. If successful, similar units will probably be installed at other LAP plants using carbon treatment of pink water.

3. Disposal of Outdated Explosives

Large shells are drilled, then heated to remelt the explosives in order to empty the shell. The resultant explosives are then burned in open burning grounds. Small shells are incinerated in incinerators. At present explosive shells or the explosives are not reused.

Future disposal of outdated explosive shells will be carried out at Hawthorne, Nevada. Hawthorne is scheduled to be operational in 1980. This facility will be the primary location for all demilitarization of outdated material. It is also anticipated that there will be more effort expended on the reuse of outdated explosives and shells in the future.

E. REFERENCES

- Adams, A.P. and Whiting, J.H. (1976), "The Effect of Hexamethylenetetramine and Copper Ion on the Nitrification-Denitrification of Effluents from the Manufacture of RDX and HMX," TECOM-05-CO-523-ECP-025.
- Bachmann, W.E. and Sheehan, J.C. (1949), "A New Method of Preparing the High Explosive RDX," *J. Amer. Chem. Soc.*, 71, 1842.
- Bender, E.S.; Robinson, P.F.; Riader, D.D.; Moore, M.W.; Thornton, W.D. and Asaki, A.E. (1977), "Preliminary Environmental Survey of Holston Army Ammunition Plant, Kingsport, Tennessee, April, 1976," Report No. ARCSL-TR-77053.
- Buckley Jr., W.J.; Jackson Jr., B.; Szachta, J.B. and Layne, W. (1977), "Effective Regeneration of Activated Carbon for Munition Wastewater Treatment" in Meeting Report - Military Applications of Environmental Research and Engineering, December 7-8, 1977, Edgewood Laboratory Area, Aberdeen Proving Ground, Maryland.
- Campbell, D.L. (1976), "Hexamine Recovery at Holston Army Ammunition Plant," ADA 024 747.
- Clark, Dietz and Associates-Engineers, Inc. (1974), "Industrial Waste Treatment Facilities, Holston Army Ammunition Plant," Vol II.
- Epstein, J.; Sommer, H.Z. and Hackley, Jr., B.E. (1976), "Environmental Quality Standards Research of Wastewaters of Army Ammunition Plants," Project MRDC (SGO), 3728.
- Hash, R.L. (1978). Private Communication.
- Hash, R.L.; Evans, J.R. and Simerly, P.V. (1977), "Pilot Plant Investigation for Treatment of Explosive Contaminated Wastewater from Holston Army Ammunition Plant," Report No. HDC-32-77, Contract No. DAAA 09-73-C-0079.
- HDC (1978), Summary of Sampling and Analysis Data, Holston AAP.
- Heidelberger, W. (1971), "Holston Army Ammunition Plant Pollution and Abatement Plans," AD890 239L.
- Huff, B.L.; Duckert, W.D.; Barding, P.G.; Wheeler, J.H. and Bogardus, R.B. (1975), "Aquatic Field Surveys at Radford, Holston, Volunteer and Milan Army Ammunition Plants, Volume II-Holston," Contract No. DAMD17-74-C-4138.
- Jackson, R.A.; Green, J.M. and Hash, R.L. (1976), "Nitramine Removal Study," Report No. HDC 22-76, Contract No. DAAA09-73-C-0079.

- Patterson, J.; Shapira, N.I.; Brown, J.; Duckert, W. and Polson, J. (1976a), "State-of-the-Art: Military Explosives and Propellants Production Industry, Volume I-The Military Explosives and Propellants Industry," PB-265-385.
- Patterson, J.; Shapira, N.I.; Brown, J.; Duckert, W. and Polson, J. (1976b), "State-of-the-Art: Military Explosives and Propellants Production Industry, Volume II-Wastewater Characterization," PB 260 918.
- Patterson, J.; Shapira, N.I.; Brown, J.; Duckert, W. and Polson, J. (1976c), "State-of-the-Art: Military Explosives and Propellants Production Industry, Volume III-Wastewater Treatment," PB-265 042.
- Small, M.J. and Rosenblatt, D.H. (1974), "Munitions Production Products of Potential Concern as Waterborne Pollutants - Phase II," AD-919 031.
- Sullivan, Jr., J.H.; Putnam, H.D.; Keirn, M.A.; Swift, D.R. and Pruitt, Jr., B.C. (1977), "Aquatic Field Surveys at Holston Army Ammunition Plant, Kingsport, Tennessee," Contract DAMD-17-75-C-5049.
- Tatyrek, A.F. (1976), "Treatment of TNT Munitions Wastewaters: The Current State-of-the-Art," Technical Report 4909, Picatinny Arsenal.
- USAEHA (1971), "Waste Flow Characterization, Area B, Holston Army Ammunition Plant, Kingsport, Tennessee," Letter Report to Commanding Officer, U.S. Army Construction Engineering Research Laboratories, ATTN Chief, Electromechanical Systems Laboratory.
- USAEHA (1972), "Water Quality Engineering Special Study No. 24-021-71/72; Industrial Wastewater, Holston Army Ammunition Plant, Kingsport, Tennessee, 19 March - 28 June 1971."

AD

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

HEXAMINE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

HEXAMINE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an
official Department of the Army position unless so design-
ated by other authorized documents.

SUMMARY

Hexamine is one of the starting materials used in the production of the explosives RDX and HMX at Holston Army Ammunition Plant. This chemical is purchased from civilian manufacturers. Army purchase of hexamine has averaged 31 million lb per year over the last eight years with a high and low yearly purchase of 65 million lb and 4 million lb. Over the same period civilian production of hexamine has averaged 88 million lb/year with a high yearly production of 145.9 million lb and a low of 47.4 million lb. As the Army's need for RDX and HMX has declined during peacetime, their purchase of hexamine has also declined. In 1975, Holston AAP purchases only accounted for 32% of the civilian production of hexamine. However, if full mobilization were to occur, the Army's needs would be ~ 75% (154 million lb/year) of the current civilian production capacity.

Hexamine is a reactive heterocyclic fused ring compound produced by the condensation of formaldehyde and ammonia. Currently, there are 6 civilian manufacturers of hexamine with a total capacity of 154 million lb/year. The major civilian use of hexamine is as a methylenating agent for crosslinking in thermosetting phenolic resins. It is also used as an intermediate in the production of nitrilotriacetic acid, as an accelerator in the rubber industry, a urinary antiseptic, etc.

Due to the use of hexamine as a urinary antiseptic, its mammalian toxicological properties have been thoroughly studied. Hexamine exhibits low toxicity in acute doses (LD50 mice is 9200 mg/kg). Chronic studies with mice, rats and dogs showed no effects at low doses and only slight growth rate reduction at higher doses. Early reports of carcinogenesis due to hexamine have been disproved. No mutagenic effects were found in mammals. However, increased perinatal deaths and growth retardation were noted in beagle pups whose mothers received high doses of hexamine (1250 ppm in feed).

In the environment hexamine itself is relatively non-toxic to aquatic organisms and plants (96 hr LC50 for fathead minnows is > 2000 ppm). However, under acid conditions or microbial attack, hexamine breaks down into ammonia and formaldehyde. Formaldehyde is highly toxic to aquatic organisms (96 hr LC50 for fingerling bass is 18 ppm). Several microorganisms, mainly *Pseudomonas* sp. are capable of degrading formaldehyde, and it gradually disappears from the aquatic environment.

Some pollution from hexamine occurs in the production. Most of the manufacturers recycle their production water; however, some concentrate the water and dump it into the municipal sewage treatment plants. Microorganisms in these sewage plants should efficiently degrade the hexamine. Pollution of hexamine itself from civilian usage is almost non-existent. Therefore, the actual pollution of hexamine from the civilian sector is minor.

Holston AAP is, however, a large polluter of hexamine. Approximately 30 lb per day enter the Holston River from each C-Building (Hexamine Mixing Buildings) in operation. When the A-1 Building still is in operation, ~ 21,000

gallons per day of water containing 2000 ppm hexamine is discharged into Arnott Branch and the Holston River. Concentrations of hexamine in Arnott Branch could reach 5 ppm. Ammonia and formaldehyde concentrations from breakdown of hexamine could be as high as 6.9 ppm and 2.6 ppm. These concentrations are above the safe levels for protection of the aquatic environment.

Any further literature evaluation studies on hexamine general mammalian toxicity should be a low priority. If pregnant female workers are exposed to hexamine, additional evaluation of teratogenic effects should be undertaken. Aquatic toxicity studies of hexamine should also be a low priority. Instead, effort should concentrate on an effective treatment process.

Studies have shown that the biotreatment facilities scheduled for installation at Holston AAP will not handle the hexamine load from the A-1 still. One possible method for treatment of these wastes is to combine them with the discharges from the Area A stills and treat the combined effluent in an aerobic biotreatment pond. *Pseudomonas* sp. of bacteria grown from activated sludge are capable of assimilation of both these formaldehyde containing wastes. Further treatment could then be provided, if needed, by the central biotreatment facility.

FOREWORD

This report details the results of a preliminary problem definition study on hexamine. The purpose of this study was to determine the Army's responsibility for conducting further research on hexamine in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on hexamine, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Hexamine was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

TABLE OF CONTENTS

	<u>Page</u>
Summary	II-3
Forword	II-5
A. Alternate Names	II-9
B. Physical Properties	II-9
C. Chemical Properties	II-11
1. General Reactions	II-11
2. Environmental Chemistry	II-12
3. Detection and Analysis	II-13
D. Uses of Hexamine in Munitions Production	II-13
1. Purpose and Quantities Used	II-13
2. Occurrences of Hexamine in Aqueous Effluents	II-15
E. Uses in the Civilian Community	II-16
1. Production Methodology	II-16
2. Manufacturers, Production and Capacity	II-16
3. Usage	II-18
4. Future Trends	II-19
5. Documented or Speculated Occurrences in the Environment	II-19
F. Comparison of the Civilian and Military Uses and Pollution of Hexamine	II-20
G. Toxicological and Environmental Hazards	II-20
1. Effects of Hexamine on Man	II-20
2. Toxicity of Hexamine to Mammals	II-21
a. Acute Toxicity	II-21
b. Chronic Toxicity	II-21
c. Teratogenicity and Mutagenicity	II-23
d. Carcinogenicity	II-23
3. Aquatic Toxicity	II-26
4. Toxicity to Invertebrates	II-28
5. Microorganism Toxicity	II-28
6. Phytotoxicity	II-28
7. Environmental Fate	II-29
8. Availability of Literature for Phase II	II-29
H. Regulations and Standards	II-29
1. Air and Water Acts	II-29
2. Occupational Standards	II-29
3. National Cancer Institute	II-30
4. Department of Transportation	II-30
I. Conclusions and Recommendations	II-30
J. References	II-33

Table of Contents
(Continued)

LIST OF TABLES

<u>Number</u>		<u>Page</u>
1	Physical Properties of Hexamine	II-10
2	Comparison of Current Spectrometric Analytical Methods for Formaldehyde	II-14
3	Hexamine Purchase and Concurrent RDX/HMX Production	II-15
4	U.S. Hexamine Production, 1965 to 1976 in Million Pounds	II-16
5	Current Manufacturers of Hexamine	II-18
6	Chronic Toxicity of Hexamine on Mammals	II-22
7	Teratogenic and Mutagenic Effects of Hexamine	II-24
8	Carcinogenicity Studies with Hexamine	II-25
9	Toxicity of Formaldehyde to Aquatic Animals	II-27
10	Toxicity of Hexamine to Microorganisms	II-28

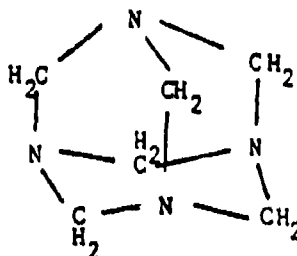
LIST OF FIGURES

<u>Number</u>		<u>Page</u>
1	Infrared Spectrum of Hexamine	II-9
2	Manufacture of Hexamethylenetetramine	II-11

II. HEXAMINE

A. Alternate Names

Hexamine possesses a heterocyclic fused ring structure:



It has a molecular formula of $C_6H_{12}N_4$ corresponding to a molecular weight of 140.1 g/mole. The utilization of hexamine by the pharmaceutical and plastics industries has resulted in a variety of alternate names for this compound. These alternate names are listed below:

CAS Registry No.: 100-97-0

Replaces CAS Registry No.(S): 7465-79-4; 11103-67-6; 15442-65-6;
15978-33-3; 56549-34-9

CA Name (9 CI): 1,3,5,7-tetraazatricyclo(3.3.1.1.3^{3,7})decane

CA Name (8 CI): hexamethylenetetramine

Wiswesser Line Notation: T66 B6 A B- C 1B I BN DN FN HNTJ

Synonyms: Aceto HMT; Aminoform; Aminoformaldehyde; Ammoform; Ammonio-formaldehyde; Antihydral; Cystogen; Duirexol; Ekagon H; Formamine; Formin; HEXA; Herax UTS; Heterin; Hexa-flo-pulver; Hexaform; Hexamethylenamine; Hexamine; Hexasan; HMTA; Methenamin; Methenamine; Preparation AF; 1,3,5,7-tetraazadamantane; Uramin; Uratrine; Uritone; Urodeine; Urotropin; Urotropine; Xametrin

B. Physical Properties

The physical properties of hexamine are presented in Table II-1. The infrared spectrum of hexamine is shown in Figure II-1.

Table II-1. Physical Properties of Hexamine*

Physical Form @ 20°C:	solid powder
Color:	white
Odor:	mild ammoniacal
Taste:	sweet
Crystalline Form:	rhombic dodecahedrons when pure
M.P.:	sublimes at 260-263°C with partial decomposition sublimes at 230-270°C in vacuum in presence of hydrogen
B.P.:	sublimes
Crystal Density:	1.35 g/cc @ 20°C 1.331 g/cc @ -5°C
Flash Point:	250°C closed cup
Flammability:	Burns with smokeless flame when exposed to fire
Autoignition Temperature:	> 370°C
Heat of Combustion:	-7400 cal/g
Solubility:	water - 150 g/100 g @ 20°C 46.5 g/100 g @ 25°C methanol - 7.25 g/100 g @ 20°C ethanol - 2.89 g/100 g @ 20°C carbon tetrachloride- 0.85 g/100 g @ 20°C chloroform - 13.4 g/100 g @ 20°C ethyl ether - 0.6 g/100 g @ 20°C precipitates from aqueous ammoniacal solutions

*Data taken from the following references:

Hawley, 1977; Windholz, 1976; Sax, 1976; Seidel, 1928;
Walker, 1975.

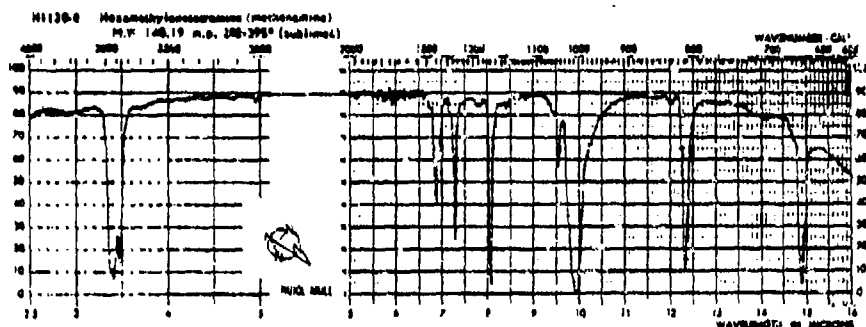
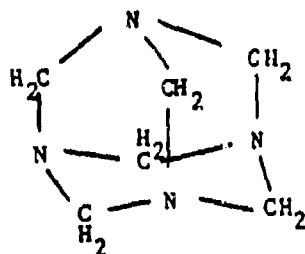


Figure II-1. Infrared Spectrum of Hexamine (Pouchart, 1970).

C. Chemical Properties

1. General Reactions

Hexamine possesses a high degree of symmetry similar to a tetrahedron.



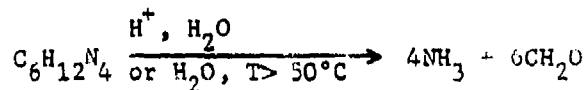
Hexamine



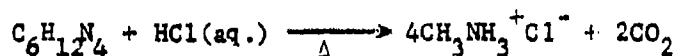
Tetrahedron

A direct result of this symmetry is the equivalence of the skeletal bonds. In spite of the apparent complexity of hexamine, it is a simple molecule.

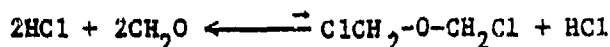
Probably one of the most important reactions of hexamine is its decomposition in acidic aqueous solution to form ammonia and formaldehyde. This reaction also occurs upon heating of aqueous hexamine solutions to temperature greater than 50°C.



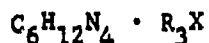
With prolonged heating of hexamine in aqueous HCl, methylamine salts are formed.



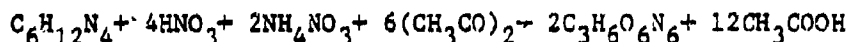
During this reaction an unfavorable equilibrium involving bis(chloromethyl) ether is established.



Hexamine forms crystalline salt with both inorganic and organic acids. Addition products are formed with many halogenated organic compounds. These addition compounds form crystals having the following formula:



Hexamine can be nitrated, nitrosated or acetylated under anhydrous conditions to form s-triazine derivatives. This type of reaction is the basis for RDX/HMX synthesis by the Bachmann process. In this procedure, ammonium nitrate and acetic anhydride are added to the reaction mixture. The result is a doubling of the stoichiometric yield of RDX over straight nitration (Fieser and Fieser, 1967).



Most other synthetic, industrial, and medicinal chemistry of hexamine takes advantage of hexamine's ease of hydrolysis. It is used as a convenient source of *in situ* formaldehyde, ammonia, or one nitrogen fragments.

2. Environmental Chemistry

The most important reaction of hexamine from an environmental standpoint is its decomposition to formaldehyde and ammonia. Russian investigators (Krasovskii and Fridlyand, 1967) monitored the formation of formaldehyde in a stagnant reservoir containing 1 mg/l of hexamine at pH 6.5. They found impermissibly high levels of formaldehyde formed under these conditions. However, the effect on a flowing river such as the Holston River would be expected to be much less than that on a stagnant reservoir. Other studies also indicate that certain *Pseudomonas* species are able to assimilate formaldehyde (Kitchens *et al.*, 1976).

A potentially important environmental reaction is the formation of dinitrosopentamethylenetetramine and trinitrosotrimethylenetriamine with nitrous acid. Only laboratory evidence of the formation of these compounds is available. They have not been shown to form in the environment.

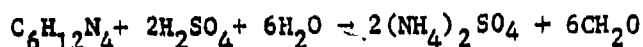
Since hexamine is not volatile, it would not be expected to be a major air pollutant. However some hexamine could enter the atmosphere as an aerosol or dust or as the formaldehyde decomposition product. No material on hexamine atmospheric photochemistry was uncovered. However, the atmospheric photochemistry of formaldehyde has been extensively studied (Purcell

and Cohen, 1967); Bufalini *et al.*, 1972). The half-life of formaldehyde in the absence of NO₂ is ~50 minutes. In the presence of NO₂, the half-life drops to ~35 minutes (Bufalini *et al.*, 1972). Thus, there is an efficient mechanism for destruction of atmospheric formaldehyde.

3. Detection and Analysis

There are no methods available for quantitative determination of hexamine which are both specific and accurate. Addition compounds with metal salts such as mercuric chloride and derivatives with iodine-iodide and picrate are specific for hexamine. However, these methods do not yield reliable quantitative results.

Hydrolysis of hexamine with excess sulfuric acid



and back titration of the acid with standard sodium hydroxide has been proposed for quantification of hexamine (Walker, 1975). This method suffers from interferences due to acids or bases in the sample and time consuming analysis procedures.

One of the most reliable methods for hexamine analysis is to determine the amount of formaldehyde released upon acid hydrolysis. This method works well if no formaldehyde or sources of formaldehyde are present in the solution. The formaldehyde released can be determined with a variety of methods. The most commonly used methods depend on the formation of a colored formaldehyde reaction product. The various colorimetric methods available and their sensitivity are presented in Table II-2. Chromotropic acid is the most widely used and accepted colorimetric method. Other methods for determining formaldehyde include

- chemiluminescence (Slawinska and Slawinski, 1975)
- atomic adsorption (Oles and Siggia, 1974)
- polarography (Whitnack, 1975).

D. Uses of Hexamine in Munitions Production

1. Purpose and Quantities Used

Hexamine is one of the starting materials for the manufacture of RDX and HMX at Holston AAP. In this process hexamine is nitrated by nitric acid/ammonium nitrate mixture in the presence of acetic anhydride and acetic acid. The production process of RDX/HMX is described in detail in Section I of this report. Historical purchase of hexamine by Holston AAP is compared with RDX/HMX production in Table II-3.

Table II-2. Comparison of Current Spectrometric Analytical Methods for Formaldehyde.

Method	max μ	Range μg/ml	Interference	Applications	References
Chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid)	580	.24-4.0	acrolein acetaldehyde	air, water, food	Bailey and Rankin, 1971
J-acid λ excite 470 6-amino-1-naphthol-3-sulfonic λ emission 520		0.001-0.2 fluorometric	acrolein, CH ₂ O polymers	tissue	Bailey and Rankin, 1971
MBTH (3-methyl-2-benzothiazolene hydrazone)	628	0.05-.92	aromatic amines, Schiff bases, azo dyes	water, air	Bailey and Rankin, 1971
p-phenylenediamine	485	0.05-2.5	SO ₂	air	Rayner and Jephcott, 1961
Schiff (rosaniline)	560	0.1	acrolein, NO ₂ acetaldehyde	air	
Schiff (pararosaniline)	560	0.01-0.05	virtually specific	air	Lyles et al., 1965
Nash (acetylacetone, ammonia)	514				Smith and Erhardt, 1975
Tryptophan	575	1-100 nanomoles/ ml	indoles, heavy metals	tissue, water	Chrastil and Wilson, 1975
Phenylhydrazine	520	.88-15			Stahl, 1969
o-aminobenzaldehyde	440	12-120	aliphatic aldehydes		Stahl, 1969
Phenyl-J-acid	560	.56-13	formaldehyde yielding compounds	air	Stahl, 1969

Table II-3. Hexamine Purchase and Concurrent RDX/HMX
Production (in Thousands of Pounds) (NDC, 1973)

	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
Hexamine Purchase	58,000	40,800	65,088	37,340	12,214	20,001	12,870	3,974.6
~ RDX Production	12,407	114,486	101,636	102,777	97,704	45,854	23,488	11,138
~HMX Production	2,639	1,865	3,533	4,787	2,502	2,460	1,391	2,249

Based on 100% yield, 0.32 lb of hexamine are needed to produce 1 pound of RDX. To produce 1 pound of HMX, 0.2023 lb of hexamine are necessary. Based on the total amounts of hexamine purchased and RDX and HMX produced during the eight year period from 1970 to 1977, the yield for RDX-HMX is ~59%. This number is in good agreement with the reported yields of 65%. Differences can be accounted for by miscellaneous products and losses of RDX, HMX in the dewatering and recyclization processes. However, ~35-40% of the hexamine ends up as unwanted by-products such as SEX, TAX, the methylamines, etc.

Current usage of hexamine at Holston AAP is ~2 million lb per month. At full mobilization, 114.8 million lb of hexamine per year (9.6 million lb per month) would be used to produce 211.7 million lb/year of RDX/HMX (17.64 million lb/month).

2. Occurrences of Hexamine in Aqueous Effluents

The only discharges of purchased hexamine occur from the C-Buildings. The hexamine discharge is from spills and building wash down. According to Green (USAEHA, 1971), 30 lb of hexamine are discharged daily in 17,000 gallons of water from each operating C-Building. At full mobilization, three C-Buildings would be mixing hexamine. Thus ~90 lb of hexamine would be discharged daily in 52,800 gallons of water from these buildings.

The hexamine effluents from the C-Building are minor compared to the hexamine discharge from the A-1 ammonia recovery still. At a feed rate of 15 gpm, this still discharges ~21,000 gallons per day to Arnett Branch (USAEHA, 1971). This effluent contains ~5,000 ppm hexamine (896 lbs of hexamine discharge per day) (Adams and Whiting, 1976). The hexamine is formed in the column by reaction of formaldehyde and ammonia in the column. This reaction is known to occur under the conditions found in the column - high pressures, temperatures and the presence of an alkali catalyst.

Currently the A-1 still operates only one week every four months. However at full mobilization, the A-1 still would operate continuously. Feed rates would probably have to be increased to 21 gpm. At this feed rate, 1250 lbs per day of hexamine would be discharged in ~30,000 gallons of water. The resulting Holston River concentrations would be 0.072 mg/l assuming full mixing.

E. Uses in the Civilian Community

1. Production Methodology

Current industrial production of hexamine uses a well established process which has remained unchanged since the late fifties. The process involves condensation of ammonia and formaldehyde. The reaction proceeds almost quantitatively according to the following equation:



The flow sheet for the manufacture of hexamethylenetetramine is presented in Figure II-2 and described below.

- (1) The reactor feed consists of ammonia gas and a 37% uninhibited formalin solution.
- (2) In the reactor, this mixture is controlled to a pH of 7 to 8 and a temperature between 30 and 50°C to prevent decomposition of the product. Temperature control is maintained by a water cooled heat exchanger. Conversion takes 4 to 5 hours.
- (3) The reactor effluent is passed into a vacuum evaporator where the product is concentrated and excess reactants removed. Addition of ammonia in this step helps to prevent decomposition of the hexamine. Temperatures are maintained at ~50°C to aid in precipitation.
- (4) The slurry from the evaporator is centrifuged, washed and sent to the drier. Drier temperatures are also maintained at 50°C or below.

The resultant material is 99% hexamine (technical grade). Recrystallization from alcohol yields USP grade (99.5%) hexamine. Total yield is 90 to 95% based on formaldehyde used.

2. Manufacturers, Production and Capacity

Historical production figures from 1965 to the present are listed in Table II-4. They show a steadily growing market until the early seventies when decreased military activity slowed the market down.

Table II-4. U.S. Hexamine Production, 1965
to 1976 in Million Pounds (U.S. Tariff Commission).

<u>1965</u>	<u>1966</u>	<u>1967</u>	<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>
49.3	78.8	84.3	96.8	97.0	76.6	47.4	95.2	100.7	145.9	61.6

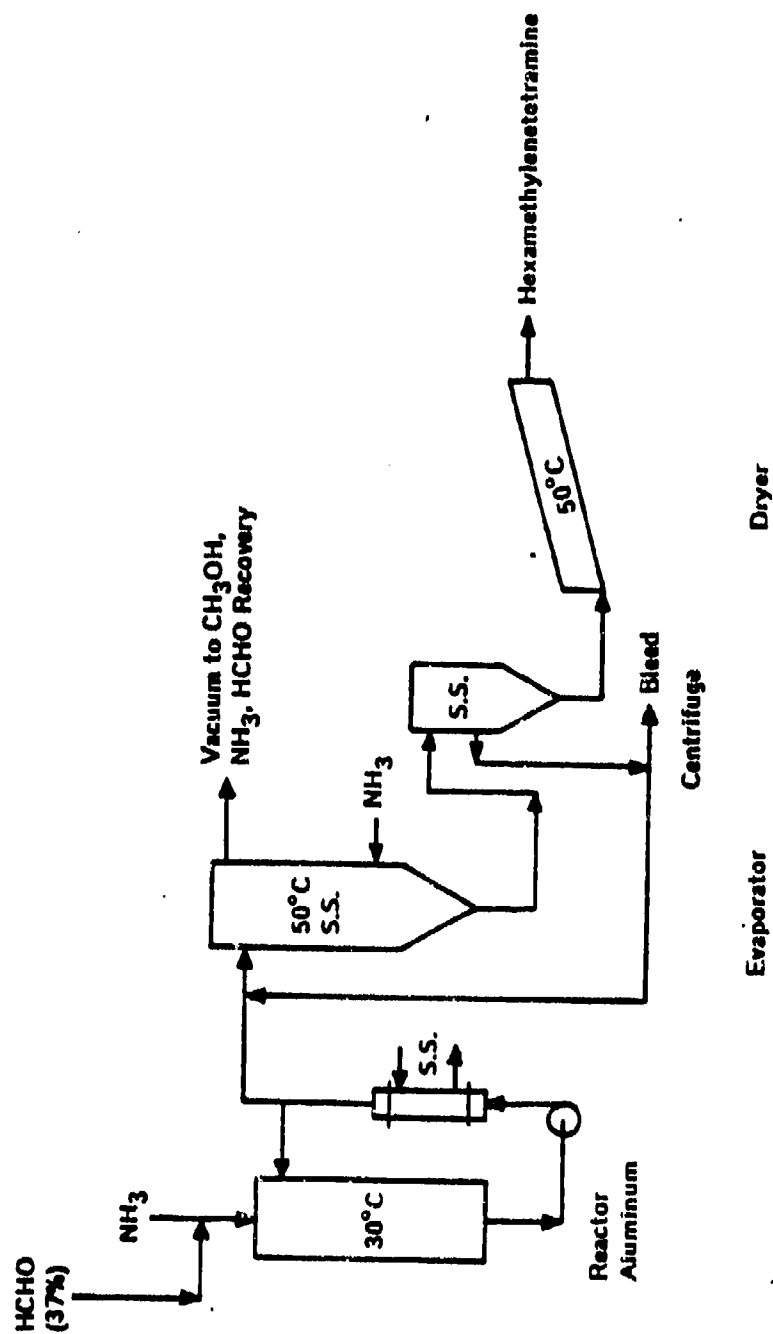


Figure II-2. Manufacture of Hexamethylenetetramine
(Sherwood, 1958)

Current manufacturers, hexamine capacities, and production locations are presented in Table II-5.

Table II-5. Current Manufacturers of Hexamine (S.R.I., 1977)

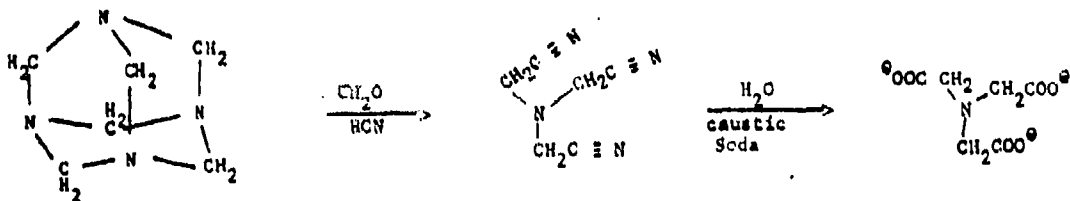
<u>Manufacturer and Location</u>	<u>Capacity (10⁶ lb/year)</u>
Borden, Fayetteville, NC, Demopolis, Ala.....	36
Grace, Nashua, N.H.....	30
Hooker, North Tonawanda, N.Y.....	28
Plastics Engineering, Sheboygan, Wis.....	8
Tenneco, Fords, N.J.	22
Wright Chemical, Riegelwood, N.C.	31
Total	155

In 1974, E.I. duPont closed a plant at Belle, West Virginia with a 12 million pound per year capacity. Union Carbide Chemicals withdrew from the hexamine market in 1976, closing a 10 million pound facility at Bound Brook, N.J. W. R. Grace manufactures hexamine solely for captive use in the synthesis of nitrilotriacetic acid, an industrial chelating agent. Borden Chemical, Hooker and Plastics Engineering use hexamine in the manufacture of phenolic resins. These manufacturers also sell hexamine. Wright Chemical and Tenneco sell 100% of their hexamine into the merchant market.

3. Usages

The major use of hexamine in the civilian sector is in the manufacture of phenolic resins. It is used as a methylenating agent for cross-linking in thermosetting resins. These phenolic resins are widely used in the automobile and housing industries. This use accounts for 64% of the hexamine currently manufactured in the United States. RDX/HMX production accounts for 18% and the miscellaneous uses described below account for 18%. (S.R.I., 1977)

Hexamine is used as a chemical intermediate in the manufacture of nitrilotriacetic acid (NTA). Hexamine is treated with HCN in the presence of formaldehyde, followed by hydrolysis to yield NTA salts



NTA is used as a chelating agent and a builder in synthetic detergents.

Hexamine is also used as an accelerator in the rubber industry, a urinary antiseptic, a metal corrosion inhibitor, in solid fuel tablets, as a

fungicide additive to prevent chemical "peel burn" in citrus fruits, and in the textile industry for improved shrinkproofing, dye fastness, and fiber elasticity.

4. Future Trends

As the housing and automobile markets improve, civilian demand for phenolic resins should increase. These resins currently account for the majority of hexamine used in the civilian community and an increase in their use will significantly increase hexamine consumption.

Recently developed applications of hexamine include:

- use as a deactivator for carriers used in insecticide dust formulations
- as a complex former in the recovery of phenolic compounds from coal tars and oils
- in the manufacture of catalyst spheres for gasoline reformation
- as an additive to lignin-reinforced rubber

Regardless of any foreseeable increase in civilian demand for hexamine, the severely reduced military use during peace time guarantees substantial spare capacity in the future.

5. Documented or Speculated Occurrences in the Environment

Environmental discharge of hexamine from manufacture or use might occur as aqueous hexamine or formaldehyde and ammonia. Discharges under acidic conditions or at temperatures above 50°C will occur totally as formaldehyde and ammonia. Discharge levels from the manufacture and use of hexamine were determined through contracts with the manufacturers.

- W. R. Grace claims essentially quantitative transformation of hexamine to NTA with zero hexamine loss.
- Wright Chemical uses a closed circuit water system which recaptures all spills and evaporator entrainment of hexamine.
- Borden Chemical has no on site water treatment. Their wastewater is passed through a pre-treatment stage involving concentration and then is sent directly to the municipal sewer system.
- Plastics Engineering claims a 95% yield of hexamine based upon formaldehyde used. This is identical with the reported effectiveness of the process (Lowenheim and Moran, 1975). The discharge water from the evaporator is passed through a condenser. The condenser is vented to the air. The condenser effluent is

passed onto the municipal sewage treatment. Ammonia can be smelled in the effluent.

F. Comparison of the Civilian and Military Uses and Pollution of Hexamine

In past years, the utilization of hexamine in RDX/HMX manufacture has accounted for 40-70% of the civilian production. This percentage has dropped significantly. For example in 1975, HAAP purchases of hexamine only accounted for about 32% of the civilian production. However, at full mobilization HAAP needs would be ~75% of the civilian production capacity of hexamine. If the new X-Facility goes into production, the amount of hexamine needed for military purposes will probably increase.

HAAP is also one of the major polluters of hexamine. Many of the civilian processors report no process losses. The civilian manufacturers who do release hexamine into the environment, usually release it through a municipal sewage treatment system. The usage of hexamine in resins should not result in any significant loss of this chemical to the environment.

G. Toxicological and Environmental Hazards

1. Effects of Hexamine on Man

Hexamine has been used by the medical professions as a urinary antiseptic since 1894. The official drug title for hexamine is Methenamine, N.F. When used as a therapeutic agent, methenamine is administered orally at a dosage of 4 to 5 g per day. The drug is absorbed by the intestine unaltered, circulated in the blood and excreted in the urine. If the urine is acidic, the drug decomposes to formaldehyde and ammonia. The released formaldehyde is the active agent being particularly effective against gram-negative organisms. In order to assure the breakdown of methenamine in the urine, acid forming compounds are administered simultaneously. Premature dissociation in the stomach is prevented by enteric-coated tablets.

Many clinical studies involving methenamine in combination with acid forming compounds have been reported in the literature. Seneca *et al.* (1967) reported only occasional gastro-intestinal intolerances in patients given methenamine hippurate orally. There has been no reported evidence of liver damage, bone marrow depression or peripheral neuritis with the recommended dosage. With an excessive dosage, gastro-intestinal irritation and bladder irritation occur from the higher concentration of formaldehyde. Andelman (1965) studied over 300 pregnant women with bacteriuria treated with methenamine hippurate and found that no toxicity was experienced. Children subsequently born experienced no abnormalities (Andelman, 1965). Riker Laboratories (1964-65) confirmed the low toxicity of methenamine hippurate in studies with rats, rabbits and dogs. No teratogenic effects were found. Gibson (1970) evaluated methenamine hippurate in 29 cases of urinary tract infections. Only two of the twenty-nine patients experienced side effects such as nausea when given 2 g

doses daily for four weeks. No other side effects were reported. Gerstein *et al.* (1968) studied the effects of methenamine hippurate in the treatment of chronic urinary tract infections. Eighteen patients were involved in this study, and received 4 g daily doses for up to 16 months. Five of the 18 patients experienced possible adverse reactions. Two patients experienced nausea and vomiting on 4 grams per day, but were able to tolerate 2 gms per day. One patient experienced nausea but returned to normal without any change in the drug dosage. One patient developed an erythematous rash which disappeared. Another patient developed a rash 6 weeks after treatment initiation. This rash continued until the drug was discontinued.

An accidental overdose of methenamine mandelate was reported by Ross and Conway (1970). A 2-1/2 year old boy ingested at least 8 g of the drug and developed hemorrhagic cystitis. The patient recovered completely without specific treatment.

In addition to its use as an urinary antiseptic, hexamine has also been reported to be effective in treatment of acute phosgene poisoning. The action of hexamine appears to be the combination with the active CO group of phosgene to prevent progressive pulmonary edema (Stavrakis, 1971).

2. Toxicity of Hexamine to Mammals

a. Acute Toxicity

Acute toxicity studies on hexamine show that it is relatively non-toxic to rats and mice. The reported LDLo for oral administration to mice is 512 mg/kg (Chemical Biological Coordination Center, 1957). For intravenous administration to rats, an LD50 of 9200 mg/kg was reported (NIOSH, 1976).

b. Chronic Toxicity

Watanabe and Sugimoto (1955) reported that hexamine caused tumors in rats when subcutaneously injected with aqueous hexamine-formic acid solutions. This report caused concern among world health organizations over the danger from the use of hexamine as a food preservative and a urinary antiseptic. Since Watanabe's study, several other investigators have evaluated the effects of hexamine over long exposure periods. These studies are summarized in Table II-6. Della Porta *et al.* (1968) conducted a well controlled long term (lifetime) oral feeding study in mice and rats. They found no adverse effects on the growth or survival for 0.5 and 1% aqueous hexamine solutions. With 5% solutions some minor growth rate retardation was observed as well as a small decrease in lifespan. Brendel (1964) observed no adverse growth, behavior, mortality or histopathological effects in albino rats fed 200-400 mg hexamine daily for one year. They did, however, observe a yellow coloration of the fur. This coloration is probably due to the reaction between formaldehyde and kynurenine (Kerwitz and Welsch, 1966).

Table II-6. Chronic Toxicity of Hexamine on Mammals

Subject	Number of Animals	Route	Concentration	Duration	Daily Intake (g/kg/day)	Response	Reference
Mouse-CTH	50 M; 50 F	oral	0.5	60 weeks	1.25	No apparent effects	Della Porta <i>et al.</i> , 1968
Mouse-CTH	96 M; 102 F	oral	1.0	60 weeks	2.5	No apparent effects	"
Mouse-CTH	29 M; 50 F	oral	5.0	30 weeks	12.5	Slight growth rate and survival rate reduction	"
Mouse-SUK	29 M; 27 F	oral	1.0	60 weeks	2.5	Slight growth rate reduction	"
Mouse-C3H/c	49 M; 44 F	oral	1.0	60 weeks	2.5	No apparent effects	"
Rat-Wistar	48 M; 48 F	oral	1.0	104 weeks	2.0-1.5 M 2.5-2.0 F	No apparent effects	"
Rat-Wistar	12 M; 12 F	oral	5.0	104 weeks		No apparent effects	"
Rat	15 M; 15 F	oral	0.4 g/ml	6 weeks		Yellow coloration of the fur	Brendel, 1964
Rat-Wistar	16 M; 16 F	oral		lifetime	100 mg/kg	No adverse effects	Narvig <i>et al.</i> , 1971
Mouse-CTH	39 M; 44 F	s.c.	30% w/v	5 Alternate days starting at 10 days of age	25 g/kg total	No apparent effects	Della Porta <i>et al.</i> , 1968
Rat-Wistar	20 M; 20 F	s.c.	30% w/v	5 Alternate days starting at 10 days of age	25 g/kg total	No apparent effects	"
Dog-beagle	9 pregnant female			56 days	15 mg/kg/day	No adverse effects on female or pups	Hurni and Ohder, 1973
Dog-beagle	10 pregnant females			56 days	31 mg/kg/day	"	"

In a more recent study by Natvig *et al.* (1971), no effects on rats were observed from daily ingestion of 100 mg/kg body weight. Life-span, mean body weights, relative organ weights, muscular activity and palatability of food containing hexamine were observed during this study.

c. Teratogenicity and Mutagenicity

Teratogenicity and mutagenicity of oral doses of hexamine in mammals have been studied. These studies are summarized in Table II-7. In these cases, effects upon the mother, the pregnancy or the placenta were not observed. Hurni and Ohder (1973) observed beagle pups whose mothers were fed hexamine beginning on the fourth day after mating and continuing to the 56th day after mating, just prior to delivery of the pups. Of the pups observed, none showed any effects such as structural or skeletal malformations. Pups from mothers receiving high doses of hexamine (1250 ppm in feed) showed increased perinatal mortality and growth retardation. Other groups, receiving low doses of hexamine (600 ppm), were essentially normal. Some of the pups were returned to the breeding colony and as of the time of the report, their offspring had shown no abnormalities in number or structure. These studies failed to indicate any gross teratogenic or mutagenic response to hexamine. However, the increased perinatal deaths with high doses may be the result of some histological changes to the embryo *in utero*.

d. Carcinogenicity

Watanabe and Sugimoto (1955) described the induction of tumors at the site of injection of hexamine in eight out of fourteen animals surviving the three month dosage period (injections of 1.0 or 2.0 ml of 23% hexamine twice weekly). Simultaneous subcutaneous injections of 0.5 ml of 0.1% formic acid were also made. These studies were on a small group of rats. No controls were mentioned.

Della Porta *et al.* (1968) have reported a large and well controlled study on the carcinogenicity of hexamine. Their results are summarized in Table II-8. These life-time studies were conducted on one rat strain and 3 strains of mice (one outbred and two inbred). Hexamine was administered in drinking water. The dosing period was from 30-60 weeks in mice and 104 weeks in rats, using doses of hexamine which caused no toxicity and minimal depression in weight gain. No evidence of carcinogenicity was found, a conclusion which agrees with Brendel's 1964 study on rats given 400 mg/day hexamine orally for 1 year.

The only data purporting to demonstrate that hexamine is carcinogenic are Watanabe's uncontrolled studies in rats dosed repeatedly with high concentrations of this substance by subcutaneous injections. The doses and injection volumes used caused irritation and scarring at the injection site. It is well known that repeated, non-specific irritation of the skin and many other organs can lead to the appearance of tumors. The lack of reported results from control animals and the fact that the route of administration is not related to common environmental modes of exposure, reduces the significance of Watanabe's studies.

Table II-7. Teratogenic and Mutagenic Effects of Hexamine

Species	Number of Animals	Route	Dosage Rate	Dosage Period	Number of Offspring	Malformations	Remarks
Rat-Nistar ^a	6 M; 6 F	Oral	1% in water daily	2 wks before mating through pregnancy and lactation weaning to 20 wks	124	None at birth	Body weight was lower than controls until 9-13 weeks old
Pigs ^b	8 bitches	Oral	15 mg/kg/day	56 days	50 (2 dead)		No structural or other malformation
	9 bitches	Oral	31 mg/kg/day	56 days	56 (10 dead)		"

^a Della Porta et al., 1970

^b Murni and Oeder, 1973

Table II-8. Carcinogenicity Studies with Hexamine

Subject Name (No.)	No. of Animals Control Test		Route	Concentration	Duration	Dose (g/kg/day)	Control		Animals without Tumors Treated		Response	Reference
	Sex	No.					Sex	No.	Sex	No.		
Group 1	M	23	Oral	0.5%	60 wks	1.25	M	43	M	23	46	8088
	F	18	Oral	0.5%	60 wks	1.25	F	32	F	12	25	8712
	M	94	Oral	1.0%	60 wks	2.5	"	"	M	37	39	8128
	F	102	Oral	1.0%	60 wks	2.5	"	"	F	25	24	8319
Group 2	M	27	Oral	5.0%	30 wks	12.5	"	"	M	19	70	64314
	F	40	Oral	5.0%	30 wks	12.5	"	"	F	12	25	71420
	M	28	Oral	1.0%	60 wks	2.5	M	21	M	16	57	78113
	F	24	Oral	1.0%	60 wks	2.5	F	9	F	12	50	91114
Group 3	M	49	Oral	1.0%	60 wks	2.5	M	9	M	27	55	95110
	F	40	Oral	1.0%	60 wks	2.5	F	16	F	20	50	10110
Group 4	M	34	s.c.	5 g/kg x 5 days	alternate 25 g/kg total		"	"	M	19	50	9116
	F	40	s.c.	5 g/kg x 5 days	alternate 25 g/kg total		"	"	F	5	37	83110
Group 5	M	43	Oral	1.0%	104 wks	2.0-15 M	M	8	M	12	25	123113
	F	48	Oral	1.0%	104 wks	2.5-2.0 F	F	11	F	21	44	113110
Group 6	M	6	Oral	5.0%	104 wks		M	8	M	2	33	14415
	F	6	Oral	5.0%	104 wks		F	11	F	3	43	10412
Group 7	M	18	s.c.	5 g/kg x 5 days	alternate 25 g/kg total		"	"	M	8	44	150112
	F	19	s.c.	5 g/kg x 5 days	alternate 25 g/kg total		"	"	F	11	58	96110
Group 8	M	20	s.c.	1 or 2 ml of 5 or 23% + 0.5 ml .1% formic acid	5 months		"	"	"	"	"	"
	F	20	s.c.	1 or 2 ml of 5 or 23% + 0.5 ml .1% formic acid	5 months		"	"	"	"	"	"

6 died of unknown illness
8 of remaining 14
had tumors at injection site

Matanabe and Sugimoto,
1955

3. Aquatic Toxicity

Hexamine is very soluble in water and will be available to aquatic organisms. The distribution of hexamine in aquatic systems has not been studied. Preliminary acute toxicity studies with fathead minnows (*Pimephales Promelas*) found a 96 hour LC50 greater than 2000 ppm for hexamine (Warner *et al.*, 1978). These data indicate that hexamine has a relatively low toxicity to aquatic organisms.

Under acidic conditions, hexamine decomposes to ammonia and formaldehyde. The reaction has also been shown to occur under neutral conditions, although to a much lesser extent. The average pH of the Holston River is 7.4. Therefore any decomposition in the River itself would be expected to be small. However, local acidic conditions in the HAAP effluent could result in decomposition. If this were to happen, the aquatic toxicity would be that of formaldehyde. As shown in Table II-9, formaldehyde is toxic to aquatic organisms.

At current HAAP operations, only 30 lb/day of hexamine are discharged except when the Building A-1 still is running (about 1 week out of every 4 months). The concentrations of hexamine, formaldehyde and ammonia from these sources in the Holston River are estimated to be:

- No A-1 still 1.7 ppb hexamine or
 2.4 ppb formaldehyde, 0.9 ppb ammonia
- A-1 still running 54 ppb hexamine or
 84 ppb formaldehyde, 28 ppb ammonia

At full mobilization the C Buildings would be discharging 90 lb/day of hexamine and the A-1 still would be running on a continuous basis. The resulting Holston River concentration under mobilization conditions are estimated to be:

- 57 ppb hexamine or
- 78 ppb formaldehyde, 29 ppb ammonia

Most of the hexamine is discharged into Arnett Branch. This Branch has a flow of ~22 mgd. The resulting concentrations in Arnett Branch are estimated to be 5.05 ppm hexamine when the A-1 still is in operation. Total decomposition of the hexamine in the effluents could lead to formaldehyde and ammonia concentrations of 6.89 ppm and 2.60 ppm, respectively, in Arnett Branch. These numbers do not include any formaldehyde and ammonia from other sources.

EPA (1976) has recommended that the concentration of unionized ammonia not exceed 0.02 mg/l to protect aquatic organisms. At pH 7.5 and a temperature of 20°C, total ammonia concentration ($\text{NH}_3 + \text{NH}_4^+$) would be 2.3 mg/l (EPA, 1976). This total ammonia concentration corresponds to total decomposition of 4.5 mg/l of hexamine.

Table II-9. Toxicity of Formaldehyde to Aquatic Animals

<u>Species</u>	<u>Duration hrs.</u>	<u>LC50 mg/l</u>	<u>Reference</u>
Rainbow Trout <i>Salmo gairdneri</i>	48	50	Kemp et al., 1973
Brown Trout <i>Salmo trutta</i>	48	50	"
Pompano (Juvenile) <i>Trachinotus carolinus</i>	96	69.1-74.9	"
Striped Bass (fingerling) <i>Morone saxatilis</i>	96	18	"
Flounder <i>Platichthys flesus</i>	48	100-330	"
Brown Shrimp <i>Crangon crangon</i>	48	330-1000	"

In order to protect aquatic organisms, the recommended aquatic concentration is often determined by applying a 0.05 factor to the 96 hr LC50 for the most vulnerable species (striped bass). Employing this factor, the maximum safe level for formaldehyde would be 0.9 mg/l, corresponding to total decomposition of 1.75 mg/l of hexamine. Thus, when the A-1 still is in operation, HAAP output of nascent formaldehyde and ammonia from the hexamine discharge is probably above safe levels for protection of the aquatic environment.

4. Toxicity to Invertebrates

The 48 hour EC50 of *Daphnia magna* is greater than 8000 mg/l (Warner *et al.*, 1978). Thus hexamine under stable conditions is significantly less toxic to *Daphnia magna* than formaldehyde (EC50 ~ 2 mg/l, Kitchens *et al.*, 1976).

5. Microorganism Toxicity

Hexamine has been shown to have a bacteriostatic effect on certain microorganisms in concentrations ranging from less than 100 mg/l to more than 4000 mg/l as shown in Table II-10. The bacteriostatic action is due to the breakdown of hexamine to formaldehyde and ammonia either by acidic conditions or bacteria degradation. As the formaldehyde concentration increases, the microorganisms are killed by the highly toxic formaldehyde.

Table II-10. Toxicity of Hexamine to Microorganisms

<u>Species</u>	<u>Concentration</u>	<u>Effect</u>	<u>Reference</u>
<i>Mycobacterium tuberculosis</i>	250	Antibacterial	Schraufstatter, 1950
<i>Trichophyton gypseum</i>	62.5	"	"
<i>Torulopsis minor</i>	125	"	"
<i>Staphylococcus aureus</i>	>4000	"	"
<i>Salmonella paratyphi</i>	>4000	"	"

In spite of the toxicity of hexamine and the resulting formaldehyde to most microorganisms, there are some microorganisms that are capable of utilizing these compounds. For example, certain *Pseudomonas* species efficiently utilize formaldehyde as a carbon source and *Penicillium* and *Polytrechum* prefer hexamine to ammonium nitrate.

6. Phytotoxicity

Nicholas and Nicholas (1922) grew beans in a culture media containing hexamine. At concentrations below 0.25 g/l the hexamine had favorable effects on the plant growth. These plants were able to use hexamine as their sole nitrogen source. However, at concentrations > 0.25 g/l a toxic effect as exhibited by retardation in the digestion of the cotyledons was observed.

7. Environmental Fate

In the environment, much of the hexamine released will be decomposed into ammonia and formaldehyde by either acidic conditions or microorganisms. This degradation will release significant quantities of formaldehyde and ammonia which could cause significant local stress on the aquatic environment. However, these compounds will also eventually be degraded. Continuous high hexamine discharges will thus result in the depletion of sensitive aquatic species, and an increase in population of plants, microorganisms and aquatic species capable of metabolizing the hexamine and resulting formaldehyde.

8. Availability of Literature for Phase II

Due to the use of hexamine as a urinary antiseptic, toxicological studies on the compound are numerous. The effect of hexamine on the environment has been studied to some extent. Therefore, there appears to be ample literature on hexamine for a detailed Phase II analysis.

H. Regulations and Standards

1. Air and Water Acts

There are no air and water regulations specific for hexamine. However, there is a water quality criterion for ammonia of 0.02 mg/l (as unionized ammonia) for protection of freshwater aquatic life (EPA, 1976). Since hexamine is degraded by microorganisms and acidic environment to ammonia and formaldehyde, this criterion applies indirectly.

Hexamine is listed in the EPA "Toxic Substances Control Act - Candidate List of Chemical Substances." However, there are no immediate plans for any definitive studies or regulations on hexamine.

2. Occupational Standards

There are no recommended threshold limit values for hexamine itself. Recommended U.S. TLVs for formaldehyde and ammonia are (American Conference of Governmental Industrial Hygienists, 1977):

formaldehyde	2 ppm or	2.5 mg/m ³
ammonia	25 ppm or	18 mg/m ³

The 2 ppm TLV for formaldehyde is also considered to be the maximum allowable concentration (MAC). Excursion above this MAC for a period up to 15 minutes may result in intolerable irritation, chronic or irreversible tissue damage, or narcosis of sufficient magnitude to increase accident proneness, impair self rescue or reduce work efficiency.

The USSR Standards for formaldehyde and ammonia in air are 0.8 ppm and 15 ppm, respectively. Czechoslovakia standards are slightly higher - 1.6 ppm for formaldehyde and 30 ppm for ammonia.

3. National Cancer Institute

Hexamine is not on the NCI Bioassay Program List (1978) to be tested for carcinogenesis. However, formaldehyde is on their list of chemicals tentatively selected for testing.

4. Department of Transportation

Hexamine is listed on the U.S. Coast Guards CHRIS List (1974). However, there are no shipping or labeling regulations for hexamine.

I. Conclusions and Recommendations

The goal of this preliminary problem definition study was to evaluate the Army's responsibility for conducting further studies on hexamine. In this report sufficient data is presented to establish the following conclusions.

1. The Army has been in the past and will be, if full mobilization should occur, the major user of hexamine. However, Army current use is only 18% of the civilian production.
2. Holston AAP is the major polluter of hexamine. The major source of hexamine discharge at HAAP being the A-1 still.
3. The currently planned biotreatment facility will not be capable of handling the hexamine and other chemicals from the A-1 still.
4. Sufficient mammalian toxicological studies have been conducted to characterize the toxicology of hexamine. The only problem area appears to be some teratogenic potential when administered in high doses throughout pregnancy.
5. The fate of hexamine in Arnett Branch and the Holston River has not been completely ascertained. However, studies to determine the fate of hexamine in the Holston area environment would be costly, and the results more of general interest than of value.

As a result of this study, it is concluded that hexamine should be a low priority for the detailed Phase II toxicological and environmental evaluation. The following research is recommended to clarify some hazards and to remove hexamine from HAAP's discharge.

1. If pregnant women are to be in daily contact with hexamine, it is recommended that the teratogenic potential of this compound be further studied. These studies should be conducted with rats using feed doses of 25, 50 and 100 mg/kg daily through pregnancy and lactation. Histopathological examination of the embryos at different states of development should be carried out. This task is necessary since

data to date indicate no gross structural changes only growth rate retardation *in utero*. If significant development alterations are observed, further studies on primate may be warranted.

2. Due to the potential danger of hexamine breakdown products to the aquatic environment, attention should be focused on elimination of this compound from HAAP effluents. Studies have shown that the currently planned biological treatment facility will not be capable of handling the effluents including hexamine from the A-1 still. One possible alternative is the combination of Area B A-1 still effluents with the Area A azeo still effluents into an aerobic biotreatment pond. An activated sludge type of system (specifically *Pseudomonas* sp.) should be capable of biodegrading these combined effluents. Further treatment, if necessary, could be provided by the central biotreatment facility.

J. References

- Adams, A.P. and Whiting, J.H. (1976), "The Effect of Hexamethylenetetramine and Copper Ion on the Nitrification-Denitrification of Effluents from the Manufacture of Hexamine RDX and HMX," *TECOM-05-CO-523-ECP-025*.
- American Conference of Governmental Industrial Hygienists (1977), *Documentation of the Threshold Limit Values for Substances in Workroom Air*, 3rd. ed.
- Andelman, M.B. (1965), "A Symptomatic Bacteriuria in Pregnancy. A Pilot Study in Lowering the Incidence of Prematurity," *Sci. Exhibit*, AMA Meeting, N.Y., June.
- Bailey, B.W. and Rankin, J.M. (1971), "New Spectrophotometric Method for Determination of Formaldehyde," *Anal. Chem.*, 43 (6), 782
- Brendel, V.R. (1964), "Untersuchungen an Ratten zur Verträglichkeit von Hexamethylenetetramin," *Arzneimittel Forschung*, 14 (1), 51.
- Bufalini, J.; Gay, Jr., B.W. and Brubaker, K.L. (1972), "Hydrogen Peroxide Formation from Formaldehyde Photooxidation and Its Presence in Urban Atmospheres," *Environ. Sci. Technol.*, 6(9), 816.
- Chemical Biological Coordination Center (1957), Summary Biological Tests, National Research Council, 3, 126.
- Chrastil, J. and Wilson, J. (1975), "A Sensitive Colorimetric Method for Formaldehyde," *Anal. Biochem.*, 63, 202.
- Della Porta, G.; Colnaghi, M. and Parmiani, G. (1968), "Non-carcinogenicity of Hexamethylenetetramine in Mice and Rats," *Ed. Cosmet. Toxicol.*, 6, 707.
- Della Porta, G.; Cabral, J.R. and Parmiani, G. (1970), "Studio Della Tossicità Transplacentare E Di Cancerogenesi in Ratti Trattati Con Esametilentetramina," *Tumori*, 56 (6), 325.
- EPA (1976), Quality Criteria for Water, EPA, Washington, D.C.
- Fieser, L.F. and Fieser, M. (1967), *Reagents for Organic Synthesis*, John Wiley and Sons, New York.
- Gerstein, A.R.; Okun, R.; Gonick, H.C.; Wilner, H.I.; Kleeman, C.R. and Morton II, M. (1968), "The Prolonged Use of Methenamine Hippurate in the Treatment of Chronic Urinary Tract Infection," *J. Urol.*, 100, 767
- Gibson, G.R. (1970), "A Clinical Appraisal of Methenamine Hippurate in Urinary Tract Infections," *Med. J. of Australia*, 1, 167.
- Hawley, G.G. (1971), *The Condensed Chemical Dictionary*, 9th ed., Van Nostrand Reinhold Co., N.Y.
- HDC (1978), Personal Communication.

- Hurni, H. and Ohder, H. (1973), "Reproduction Study with Formaldehyde and Hexamethylenetetramine in Beagle Dogs," *Fd. Cosmet. Toxicol.*, 11(3), 459.
- Kemp, H.; Little, R.; Holoman, V. and Darby, R. (1973), "Water Quality Criteria Data Book Vol. 5. Effects of Chemicals on Aquatic Life (Compilation from the Literature Dated 1968-1972)," U.S. Govt. Printing Office, Washington, D. C.
- Kerwitz, H. and Welsch, F. (1966), "Ein Gelber Farbstoff aus Formaldehyde und kynurenin bei Hexaminbehandelten Ratten,; *Nunyn-Scheidebergs Arch exp. Path Pharmac.*, 254, 101.
- Kitchens, J.F.; Casner, R.E.; Edwards, G.S.; Harward III, W. and Macri, B.S. (1976), "Investigation of Selected Potential Environmental Contaminants: Formaldehyde," Final Report, U.S. EPA, Washington, D.C., 20460, EPA-560/2-76-00g, ARC 49-5681.
- Krasovskii, G. and Fridlyand, S.A. (1967), "Experimental Basis for the Permissible Concentrations of Urotropine in Reservoir Waters," *Prom. Zagryazeniya Vodoemov*, 8, 140, from *Chem. Abstr.* 69:30017c.
- Lowenheim, F.A. and Moran, M.K., *Faith, Keyes and Clark's Industrial Chemicals*, 4th ed., John Wiley and Sons, New York.
- Lyles, G.R.; Dowling, F.B. and Blanchard, V.T. (1965), "Quantitative Determination of Formaldehyde in the Parts Per Hundred Million Concentration Level," *J. Air Pollut. Control Assoc.*, 15(3), 106.
- Natvig, H.; Anderson, J. and Rasmussen, E.W. (1971), "A Contribution to the Toxicological Evaluation of Hexamethylenetetramine," *Fd. Cosmet. Toxicol.*, 9, 491.
- NCI, "Chemicals Being Tested for Carcinogenicity by the Bioassay Program, DCCP, NCI," Feb, 1978.
- Nicolas, E. and Nicolas, G. (1922), "Action of Hexamethylenetetramine on the Higher Plants," *Compt. Rend.*, 175, 836, from *Chem. Abstr.* 17:796.
- NIOSH (1976), "Registry of Toxic Effects of Chemical Substances," Office of Research and Standards Development.
- Oles, P.J. and Siggia, S. (1974), "Atomic Absorption Method for Determining Micromolar Quantities of Aldehydes," *Anal. Chem.*, 47(7), 911.
- Pouchert, C.J. (1970), *The Aldrich Library of Infrared Spectra*, Aldrich Chemical Co., Inc.
- Purcell, T.C. and Cohen, I.R. (1967), "Photooxidation of Formaldehyde at Low Partial Pressure of Aldehyde," *Environ. Sci. Technol.*, 1(10), 845.
- Rayner, A.C. and Jephcott, C.M. (1961), "Microdetermination of Formaldehyde in Air," *Anal. Chem.*, 33(4), 627.

- Ricker Laboratories (1964-1965), Data Sheet.
- Ross, R. and Conway, G. (1970), "Hemorrhagic Cystitis Following Accidental Overdose of Methenamine Mandelate," *Am. J. of Diseases of Children*, 119(1), 86.
- Sax, N.I. (1976), *Dangerous Properties of Industrial Materials*, 4th Ed., Van Nostrand Reinhold Co., New York.
- Schraufst tter, E. (1950), "Formation of Heavy-Metal Complexes and Centibacterial Action," *Naturforsch.*, 5, 190.
- Seidell, A. (1928), *Solubilities of Inorganic and Organic Compounds*, Van Nostrand Co., Inc., New York, 1228.
- Seneca, H.; Zinsser, H.H. and Peer, P. (1967), "Chemotherapy of Chronic Urinary Tract Infections with Methenamine Hippurate," *J. Urol.*, (Baltimore) 97, 1094.
- Sherwood, P.W. (1958), "Take a Look at Hexamethenaminetetramine," *Petrol. Refiner*, 37(9), 351.
- Slawinska, D. and Slawinski, J. (1975), "Chemiluminescent Flow Method for Determination of Formaldehyde," *Anal. Chem.*, 47(13), 2101.
- Smith, R.V. and Erhardt, P.W. (1975), "Nash Determination for Formaldehyde in the Presence of Bisulfite," *Anal. Chem.*, 47(14), 2462.
- Stahl, Q.R. (1969), "Air Pollution Aspects of Aldehydes," National Technical Information Services, PB-188 081.
- Stavrakis, P. (1971), "The Use of Hexamethylenetetramine (HMT) in Treatment of Acute Phosgene Poisoning," *Industrial Medicine*, 40(4), 30.
- SRI (1977), *Chemical Origins and Markets*, 5th Ed., Stanford Research Institute, Menlo Park, CA.
- USAEHA (1971), "Waste Flow Characterizations, Area B, Holston Army Ammunition Plant, Kingport, Tennessee," Letter Report and Attachments.
- U.S. Coast Guard (1974), *Chemical Hazards Response Information System*, CG-446-2.
- U.S. Tariff Commission, Synthetic Organic Chemicals.
- Walker, J.F. (1975), *Formaldehyde*, 3rd Ed., Reinhold Publ. Corp., New York.
- Warner, M.C.; Randall, W.F.; Diehl, S.A.; Pearson, J.G. and Meier, E.P. (1978), "Acute Toxicity of Several Munition Related Compounds to *Daphnia magna*, Fathead Minnows and Green Sunfish," Draft, U.S. Army Research and Development Laboratories, Technical Report.

- Watanabe, F. and Sugimoto, S. (1955), "Study on the Carcinogenicity of Aldehyde. 2nd Report. Seven Cases of Transplantable Sarcomas of Rats Appearing in the Areas of Repeated Subcutaneous Injections of Urotropin," *Cann*, 46, 365.
- Whitnack, G.C. (1975), "Single Sweep Polarographic Techniques Useful in Micropollution Studies of Ground and Surface Waters," *Anal. Chem.*, 47(4), 618.
- Windholz, M. (1976), *The Merck Index*, 9th ed., Merck and Co., Inc., Rahway, New Jersey.

AD

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

CYCLOHEXANONE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

CYCLOHEXANONE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

"Permission for the publication herein by Sadtler Standard Spectra[®] has been granted, and all rights are reserved, by Sadtler Research Laboratories, Inc."

SUMMARY

Cyclohexanone is used by the Army as a recrystallization solvent for RDX at Holston Army Ammunition Plant (HAAP). The average purchase of this chemical over the last eight years has been ~ 762,000 lb/year. These purchases were for make-up solvent and are, therefore, representative of the amount of cyclohexanone lost. This loss is ~ 0.01 lb of cyclohexanone for every pound of RDX produced. Thus at full mobilization, Holston would purchase and presumably discharge ~ 2 million lb/year.

Holston discharges large quantities of cyclohexanone from the Recrystallization Buildings (G Buildings) and the Dewatering Building (H Building). At full mobilization discharges to the Holston River could be up to 1286 lb/day from the G-Buildings and 950 lb/day from the H-Buildings or a total of 787,000 lb/year. In addition to aqueous discharges from the recrystallization and dewatering process, air discharges also occur. About 51% of the cyclohexanone losses at HAAP are unaccounted for.

Cyclohexanone is produced by six civilian manufacturers. The current capacity is 1590 million lb/year. Two processes are used in the manufacture of cyclohexanone - air oxidation of cyclohexane and catalytic hydrogenation of phenol.

The major civilian use of cyclohexanone is as a chemical intermediate in the manufacture of nylon-66 and nylon-6. Other uses include manufacture of caprolactone for use in high impact plastics and as a solvent.

The total 1974 environmental discharge of cyclohexanone from manufacture and uses was estimated at 51.3 million pounds or about 8% of the quantity produced. Even at full mobilization, HAAP would discharge only ~ 4% (2 million lb/yr) of the total environment discharge of cyclohexanone. Thus it is not a military unique chemical.

Due to its widespread use as a solvent, the acute and chronic toxicity of cyclohexanone has been extensively studied. It is moderately toxic in acute doses by all routes of administration. Sublethal doses cause profound narcosis accompanied by central nervous system depression. Some teratogenic effects were observed on chick embryos. However, sufficient information is not available to fully assess the teratogenic potential of cyclohexanone. No carcinogenic or mutagenic studies on cyclohexanone were reported, however, it is on NCI's list of chemicals tentatively selected for testing by the bioassay procedure.

Only a few aquatic toxicity studies on cyclohexanone have been reported. These studies indicate a low toxicity of cyclohexanone to aquatic life. Degradation of cyclohexanone in the environment occurs through photochemical reactions and microbial degradation. However, the HAAP effluent undergoes a variety of transformations before it enters the environment. The presence of formaldehyde in the effluent leads to the formation of 2-hydroxymethylcyclohexanone. This compound can undergo a variety of reactions including dehydration and Diels-Alder addition. Addition reactions of two

molecules of cyclohexanone lead to formation of cyclohexanyl-cyclohexanone. The toxicology and the environmental hazards of these compounds have not been established.

As indicated by the data gathered and evaluated in this preliminary problem definition study, cyclohexanone is not a military unique compound. It is widely used throughout the civilian community and enters the environment from many civilian sources. Its mammalian and aquatic toxicological effects are low to moderate and are relatively well established. Some further work in the areas of carcinogenicity and teratogenicity is warranted. However, this work is a civilian problem.

A problem does exist with cyclohexanone in the effluent at Holston AAP. This problem is the formation of addition compounds. The toxicity and environmental hazards from these compounds require further evaluation.

FOREWORD

This report details the results of a preliminary problem definition study on cyclohexanone. The purpose of this study was to determine the Army's responsibility for conducting further research on cyclohexanone in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on cyclohexanone, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

Cyclohexanone was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

TABLE OF CONTENTS

	<u>Page</u>
Summary	III-3
Foreword	III-5
A. Alternate Names	III-9
B. Physical Properties	III-9
C. Chemical Properties	III-11
1. General Reactions	III-11
2. Environmental Reactions	III-13
3. Sampling and Analysis	III-14
D. Uses of Cyclohexanone in Army Munitions Production	III-15
1. Quantities of Cyclohexanone Used in Munitions Production	III-15
2. Occurrences of Cyclohexanone in Air and Water	III-15
a. Aqueous Effluents from RDX Recrystallization and Formulation (G-Buildings)	III-15
b. Air Effluents from the RDX Recrystallization and Formulation (G-Buildings)	III-17
c. Aqueous Effluents from RDX Dewatering (H-Buildings)	III-17
d. Holston River Concentration of Cyclohexanone	III-18
e. Material Balance on Cyclohexanone	III-18
E. Uses in the Civilian Community	III-18
1. Production Methodology	III-18
2. Manufacturers, Production and Capacity	III-20
3. Usages	III-22
4. Future Trends	III-23
5. Documented or Speculated Occurrences in the Environment	III-23
F. Comparison of the Military and Civilian Uses of Cyclohexanone	III-24
G. Environmental and Toxicological Hazards of Cyclohexanone	III-24
1. Human Exposure Studies	III-24
2. Mammalian Toxicity	III-25
a. Acute and Chronic Toxicity	III-25
b. Teratogenicity, Mutagenicity and Carcinogenicity	III-25
c. Biochemistry of Cyclohexanone	III-28
3. Aquatic Toxicity	III-29
4. Phytotoxicity	III-31
5. Toxicity to Microorganisms	III-31
6. Environmental Fate	III-32
7. Literature Availability for Phase II	III-33

Table of Contents
(Continued)

	<u>Page</u>
H. Standards and Regulations	III-34
1. Air and Water Acts	III-34
2. Occupational Standards	III-34
3. Department of Transportation	III-34
I. Conclusion and Recommendations	III-34
J. References	III-37

LIST OF TABLES

<u>Number</u>		<u>Page</u>
1	Physical Properties of Cyclohexanone	III-10
2	Historical Purchase of Cyclohexanone and Corresponding RDX Production at Holston AAP	III-15
3	Aqueous Effluents from Typical RDX Recrystallization Buildings	III-16
4	Aqueous Effluents from a Typical RDX Dewatering Building, . .	III-17
5	U.S. Cyclohexanone Production, 1965 to present	III-22
6	Current Producers of Cyclohexanone	III-22
7	Acute Toxicity of Cyclohexanone to Mammals,	III-26
8	Chronic Toxicity of Cyclohexanone	III-27
9	Excretion of Glucuronic Acids and Sulfates in 24 Hour Urine Samples of Rabbits Following Oral Administration of Cyclo- hexanone	III-29
10	Acute Toxicity of Cyclohexanone to Aquatic Organism	III-30
11	Cyclohexanone Levels in the Holston River	III-31

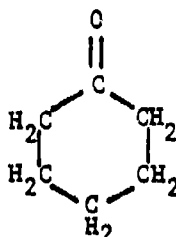
LIST OF FIGURES

<u>Number</u>		<u>Page</u>
1	Infrared Spectrum of Cyclohexanone	III-9
2	Ultraviolet Spectrum of Cyclohexanone	III-11
3	Production of Cyclohexanone by the Air Oxidation Process	III-19
4	Production of Cyclohexanone by Hydrogenation of Phenol	III-21

III. CYCLOHEXANONE

A. Alternate Names

Cyclohexanone is a cyclic aliphatic monoketone with a molecular formula of $C_6H_{10}O$ and corresponding molecular weight of 98.14 g/mole. This ketone has the following structural formula:



Other pertinent alternate names for cyclohexanone are listed below:

CAS Registry No.:	108-94-1
Replaces CAS Registry No.:	48090-95-5
CA Name (8CI):	Cyclohexanone
Wiswesser Line Notation:	L6VTJ
Synonyms:	Anon; Anone; Hexanon; Hytrol O; Keto-hexamethylene; Pimelic ketone; Pimalin ketone; Sextone

B. Physical Properties

The physical properties of cyclohexanone are listed in Table III-1. The infrared spectrum of cyclohexanone is shown in Figure III-1.

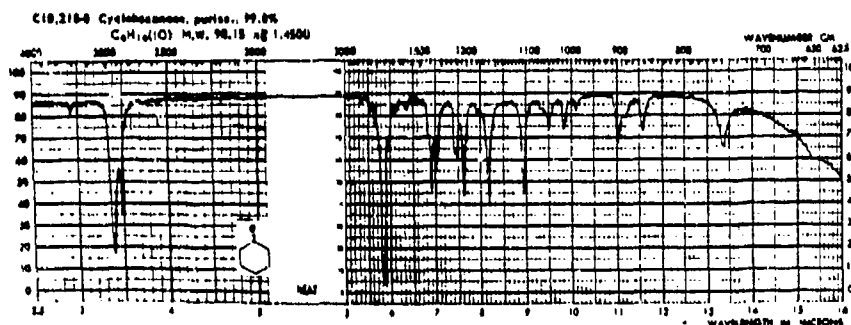


Figure III-1. Infrared Spectrum of Cyclohexanone (Pouchert, 1970).

Table III-1. Physical Properties of Cyclohexanone*.

Physical Form @ 20°C:	oily liquid	
Color:	colorless to pale yellow	
Odor:	peppermint and acetone	
M.P.:	-47°C; -45°C	
B.P.:	155.6°C @ 760 mmHg	132.5°C @ 400 mmHg
	110.3°C @ 200 mmHg	90.4°C @ 100 mmHg
	77.5°C @ 60 mmHg	67.8°C @ 40 mmHg
	52.5°C @ 20 mmHg	38.7°C @ 10 mmHg
	26.4°C @ 5 mmHg	1.4°C @ 1.0 mmHg
Vapor Pressure:	4.5 mmHg @ 25°C	
	3.95 mmHg @ 20°C	
Liquid Density, d_4^{20} :	0.9478 g/ml	
Vapor Density:	3.38 g/cc	
Refractive Index, n_D^{20} :	1.4490	
Viscosity of Liquid:	2.2 cP @ 25°C	
Flash Point:	54°C open cup	
	33°C closed cup	
Autoignition Temperature:	520-580°C	
Explosive Range:	1.1 - 8.1% @ 100°C	
Heat of Combustion (Const P):	-8570 cal/g	
Specific Heat, 15-18°C:	0.433 cal/g	
Solubility:	water - 5g/100g @ 30°C	
	15g/100g @ 10°C	
Dissolves:	Miscible with methanol, ethanol, acetone, benzene, n-hexanone, nitrobenzene, ether, naptha, xylene, ethylene, glycol, isoamylacetate, diethylamine and most organic solvents	
	water - 9.5g/100g @ 20°C Cellulose nitrate, acetate and ethers, vinyl resins, raw rubber, waxes, fats, shellac, basic dyes, oils, latex, bitumen and many other organic compounds	

*References: Kirk and Othmer, 1967; Celanese Chemical Company; Hawley, 1977; Weast, 1975; Sax, 1975; Windholz, 1976.

The ultraviolet spectrum of cyclohexanone is presented in Figure III-2. A weak absorption band is present with maxima at 280 and 276 mμ and corresponding molar absorptivity coefficients of 27 and 26, respectively.

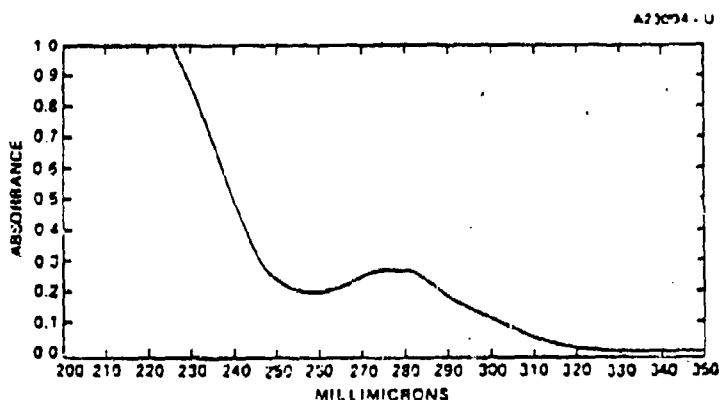
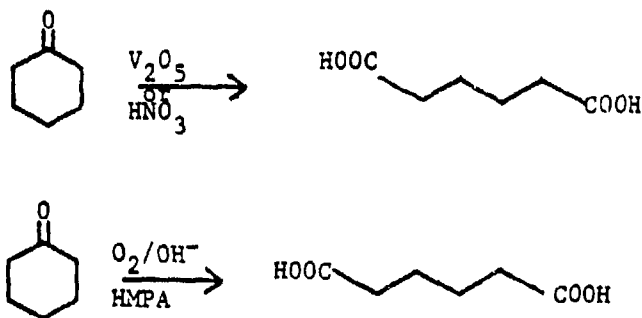


Figure III-2. Ultraviolet Spectrum of Cyclohexanone, ©Sadtler Research Laboratories, Inc. (1966).

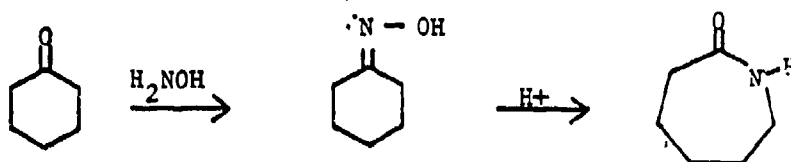
C. Chemical Properties

1. General Reactions

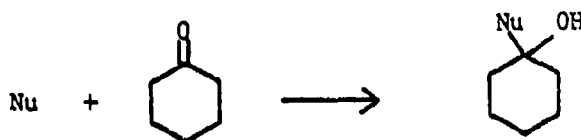
Treatment of cyclohexanone with either strong oxidizing agents in acid (March, 1968) or molecular oxygen in basic hexamethylphosphoramide (Wallace *et al.*, 1965) yields adipic acid,



Autoxidation does not occur in water. Cyclohexanone reacts with hydroxylamine to form an oxime which undergoes Beckman rearrangement (March, 1968) to ε-caprolactam used in the manufacture of nylon-6.



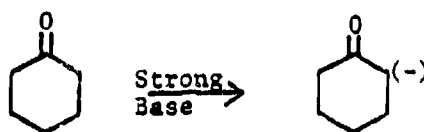
Ketones possess two chemically reactive sites. The polarity of the $\text{C}=\text{O}$ double bond causes the carbonyl carbon to be deficient in electron density and, thus, susceptible to nucleophilic attack. This general reaction scheme involves initial nucleophilic addition at the carbonyl carbon,



This addition product may either be a stable species, revert to the original ketone in a reversible equilibrium, or react further to give a new product.

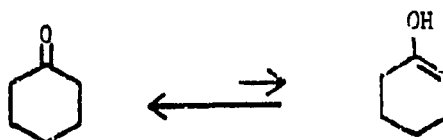
The carbon directly adjacent to the carbonyl function is the second reactive site. This carbon, called the α carbon, exhibits nucleophilic activity. In order for the α carbon to behave as a nucleophile, the ketone must undergo a transformation to either a carbanion or an enol.

The electron deficiency of the carbonyl carbon increases the Bronsted acidity (the ability to release protons) of the α carbon 10^{20} times over the other carbons. This electron deficiency allows selective removal of α protons to produce highly reactive carbanions.

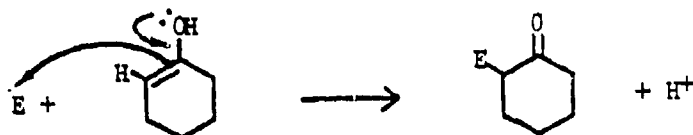


Even though ketones possess enhanced acidity over normal hydrocarbons, they are still several orders of magnitude less acidic than water. Under environmental conditions, carbanion chemistry is of little concern.

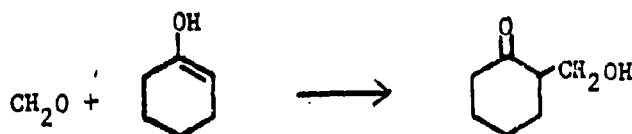
In solution, ketones exist in equilibrium with enols.



This equilibrium is referred to as tautomerism. For most ketones, cyclohexanone included, the equilibrium lies far to the left. But under acidic conditions, interconversion between tautomers occurs readily. If the small amount of enol at equilibrium reacts with another species in solutions, the tautomeric equilibrium will be driven to the right. The general reaction of enols is pictured below.



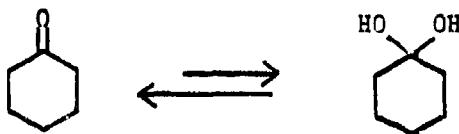
E^+ may be any electrophile. If it is a proton, then ketone is formed. Cyclohexenol will react with formaldehyde to yield 2-hydroxymethyl-cyclohexanone.



Enol chemistry is very significant in aqueous acid solutions of cyclohexanone.

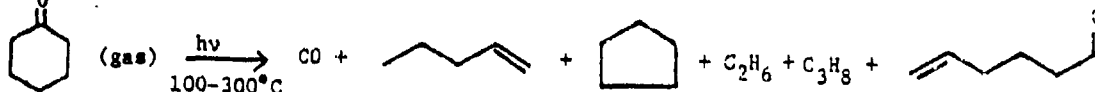
2. Environmental Reactions

Cyclohexanone is stable under normal conditions. In water it acts as neither an acid nor a base but exists in an unfavorable equilibrium with the gem-diol.

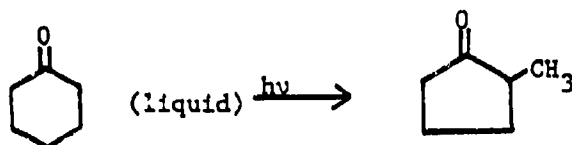
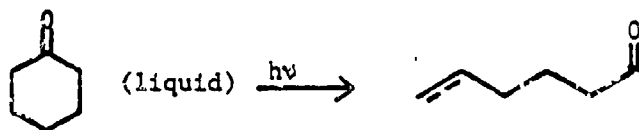


Numerous photochemical studies have been conducted with cyclohexanone. Irradiation in the vapor phase yields primarily CO, 1-pentene, and cyclopentane with lesser amounts of ethane, propane, and 5-hexenal (Srinivasan, 1963). Photolysis of pure liquid cyclohexanone has been reported to yield both 5-hexenal and 2-methylcyclopentanone (Calvert and Pitts, 1966). Irradiation of cyclohexanone in water yields hexanoic acid (Calvert and Pitts, 1966).

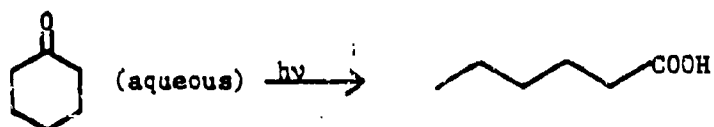
(-) Vapor Phase Irradiation



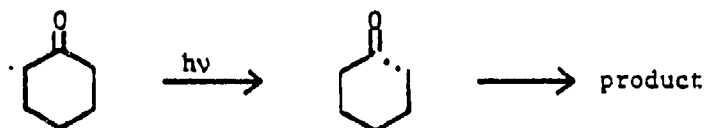
(2) Liquid Phase Irradiation



(3) Aqueous Solution Irradiation



The primary processes are believed to be excitation to an upper singlet state, followed by either homolytic cleavage to a diradical or a concerted process without radical formation (Calvert and Pitts, 1966).



Addition of molecular oxygen to the gas phase reaction shows no effects of radical scavenging indicating that cyclohexanone is not an effective initiator for photochemical smog and subjecting the existence of a diradical to question.

3. Sampling and Analysis

Gas chromatography using a flame ionization detector is considered the most sensitive and specific method of analysis of cyclohexanone. Parkes *et al.* (1976) performed analyses via direct absorption of the ketone from air samples onto Chromosorb 101 followed by heat desorption to the chromatograph. They estimated their limits of detection of 50 ppb cyclohexanone.

A portable infrared gas analyzer has been developed which obviates sample collection, an advantage for field analysis. Minimum detectable concentration of cyclohexanone by this method is reported at 0.3 ppm (Lande *et al.*, 1976).

A colorimetric field test exists which involves treatment of a sample with the diazonium salt of H-acid. The colored product is then compared with prepared standards of known concentrations. Detection limits are on the order of parts per thousand (Andrew *et al.*, 1971).

D. Uses of Cyclohexanone in Army Munitions Production

Cyclohexanone is used by the Army as a recrystallization solvent in the manufacture of RDX. When the RDX is crystallized from the acid reactant mixture, the crystals are the wrong size for further processing. Recrystallization from cyclohexanone yields crystals of the proper size.

1. Quantities of Cyclohexanone Used in Munitions Production

Table III-2 presents the historical purchase of cyclohexanone at Holston AAP and the corresponding production of RDX. Approximately 0.01 lb of cyclohexanone is added to the process for every pound of RDX produced.

Table III-2. Historical Purchase of Cyclohexanone and Corresponding RDX Production at Holston AAP.

	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>	<u>1978</u>
Cyclohexanone Purchased, lb	960,000	800,000	2,213,000	1,440,000	-	320,000	360,000	-	180,000
RDX Produced, x 1000 lb	129,407	114,486	101,636	102,777	97,704	43,354	23,488	11,133	-

Currently, Holston AAP is only operating at ~ 8% of capacity. Cyclohexanone is being added to the process at a rate of 316 lb per day. At full mobilization ~ 6000 lb per day of cyclohexanone would be used.

2. Occurrences of Cyclohexanone in Air and Water

a. Aqueous Effluents from RDX Recrystallization (G-Buildings)

Recrystallization of RDX and HMX is accomplished in the G-Buildings. Buildings G-1, 2, 7, 8, 9, 10 and 10A are used for recrystallization of RDX with cyclohexanone. Buildings G-3, 4, 5 and 6 are used for HMX recrystallization and special products formulation. The effluent from Buildings G-3, 4, 5, 6 varies with the particular product being formulated. However, cyclohexanone is usually found in the effluent.

In a study performed by Mr. Jim Green of Holston Defense Corporation, the concentrations of various solvents in the G Building catch basin influents and effluents were measured (USAEHA, 1971). The flow rates through these catch basins were also measured. The results of this study for Buildings G-2 and G-6 are presented in Table III-3. Buildings G-2 and G-6 were operating at capacity during the study. The G-2 building effluents are considered typical of Buildings G-1, 7, 8, 9, 10 and 10A. Buildings 10 and 10A operate as one building. Although there are 8 units in these buildings

Table III-3. Aqueous Effluents from Typical RDX
Recrystallization Buildings (USAEHA, 1971).

Parameter	Catch Basin Influent, mg/l	Catch Basin Effluent, mg/l
<u>Building G-2</u>		
BOD	896	339
COD	463	403
OC	234	217
IC	22	23
Cyclohexanone	215	206
Flow rate - 27,400 gallons per day (gpd)		

<u>Building G-6</u>		
BOD	332	323
COD	1240	950
OC	264	-
IC	9.7	8.0
HMX	10.6	4.4
RDX	5.0	5.0
Acetone	81	63
Cyclohexanone	587	220
Toluene	2.7	0.2
Butanol	81	63
pH	6.1	6.1

Flow rate - 136,000 gallons per day (gpd)

only 4 operated concurrently. Therefore, the effluent from RDX recrystallization at full mobilization can be obtained by multiplying that of Building G-2 by six. Approximately 164,400 gpd of process water would be discharged from these G-Buildings containing ~ 210 mg/l or 288 lb per day of cyclohexanone.

The characterization of the effluents from Buildings G-3, 4, 5, 6 are less accurate due to the variation in the products formulated in these buildings. However, as approximation of the total effluent at full mobilization, the effluents presented in Table III-3 can be multiplied by four. This approximation yields a total flow of 544,000 gpd of process water from these buildings. This water contains ~ 220 mg/l or 998 lb per day of cyclohexanone.

At full mobilization the total amount of cyclohexanone released in the aqueous effluents from the G-Buildings could be as much as 1286 lbs per day in a flow rate of 708,400 gallons per day. If no cyclohexanone is being used in Buildings G-3-6, the release of cyclohexanone could be as low as 288 lb per day.

b. Air Effluents from the RDX Recrystallization and Formulation (G-Buildings)

In addition to the aqueous cyclohexanone wastes, air emissions from the G-Buildings have been reported. These air emissions were estimated to be 95 lb/day per building (USAEHA, 1971). At full mobilization, 570 to 950 lb/day would be lost to the air depending on whether cyclohexanone is being used in the formulations buildings.

c. Aqueous Effluents from RDX Dewatering (H-Buildings)

RDX is dewatered in Buildings H-1, 2, 3, 4, 7, 8, 9 and 10. As indicated by analyses of the H-2 building effluents performed by Holston Defense Corporation, cyclohexanone is found in the waste water from the RDX dewatering process. Buildings H-5 and 6 dewater HMX and do not have cyclohexanone in their effluents. Specific parameters determined in this study are presented in Table III-4.

Table III-4. Aqueous Effluents from a Typical RDX Dewatering Building (USAEHA, 1971).

Parameter	Catch Basin Influent, mg/l	Catch Basin Effluent, mg/l
BOD	2771	-
COD	4292	-
RDX	49	33
HMX	1.5	0.7
Cyclohexanone	142	-
Acetic Acid	658	-
Flow rate - 34,800 gallons per day (gpd)		

The catch basin effluent was not monitored but can be assumed to be approximately the same as the influent. At full mobilization, Buildings H-1 2, 3, 4, 7, 8, 9 and 10 would be in full production. The total amount of cyclohexanone discharged from these buildings would be 330 lb per day in a flow of 278,400 gallons per day.

No data on air emissions of cyclohexanone from the H-Buildings was found. However, these emissions would be minor compared to those from the G-Buildings.

d. Holston River Concentration of Cyclohexanone

At full mobilization, cyclohexanone effluents to the Holston River would be as much as 1286 lb/day from the G-Buildings and 330 lb/day from the H-Buildings or a total of 1616 lb/day. The resulting Holston River concentration (assuming full mixing and a river flow rate of 2070 mgd) would be 0.10 mg/l. However, the North and South Forks of the Holston River are not thoroughly mixed until ~ 1 mile downstream from Area B. Thus, local river concentrations would be as much as 4 to 5 times this concentration.

e. Material Balance on Cyclohexanone

It is difficult to perform a material balance on cyclohexanone over a one-year period because this solvent is bought in bulk and stored until needed. A more meaningful balance can be obtained over an eight-year period. During the eight-year period from 1970 to 1977, a total of 6,095,000 lb of cyclohexanone were purchased. The average mobilization over this period was 41%. Thus, an average of 370,325 lb/year would be expected to be lost to air and water. However, an average of 761,875 lb/year were used. Thus about 51% of the cyclohexanone losses are unaccounted for.

Other sources for additional cyclohexanone losses include

- water from the recrystallization decanter contains about 0.1% cyclohexanone. This water is hauled to the burning ground (USAEHA, 1971)
- solvent in the final product
- losses to air from the dewatering operations
- losses during the incorporation step
- chemical reaction in the effluent streams.

E. Uses in the Civilian Community

1. Production Methodology

Two synthetic processes are currently used by industry to produce cyclohexanone. The catalytic air oxidation of cyclohexane is the most widely used process. A schematic of the air oxidation reaction system is shown in Figure III-3.

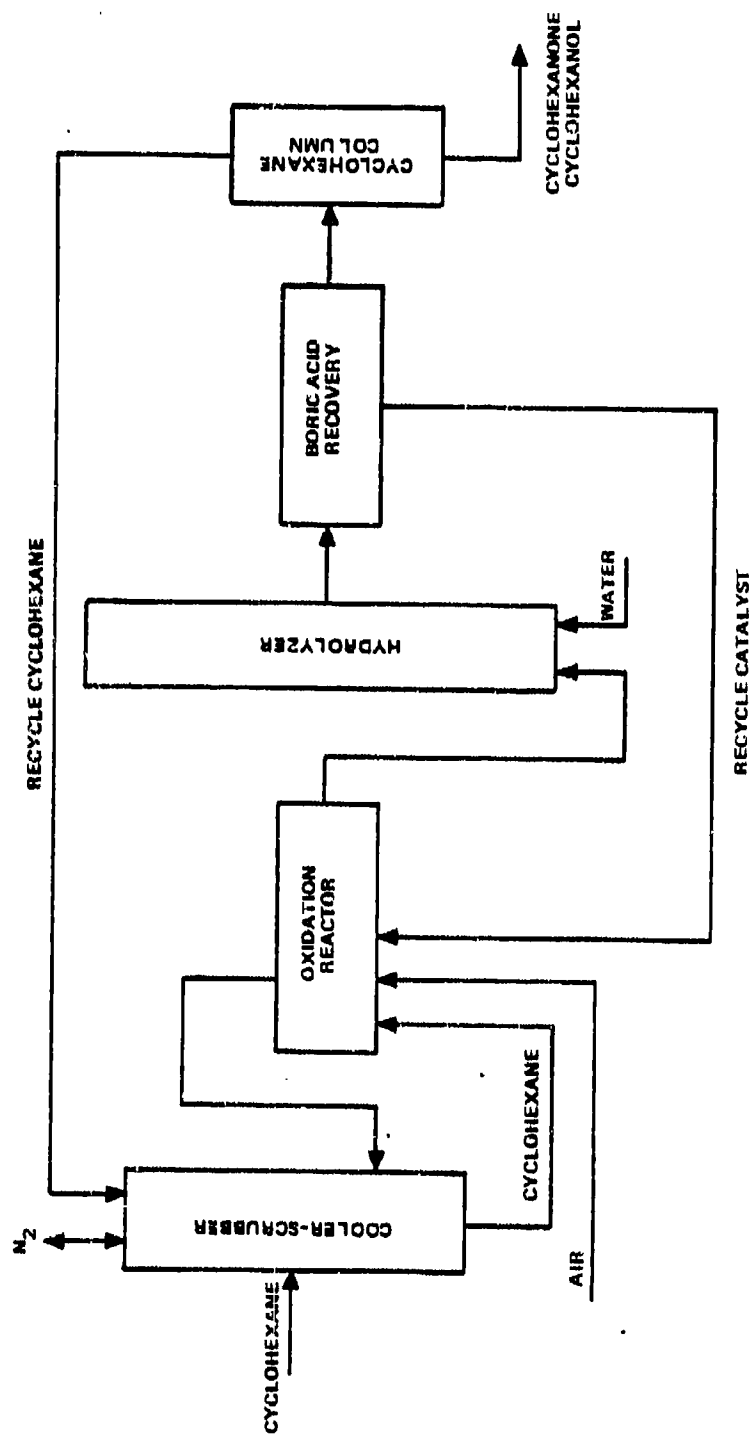
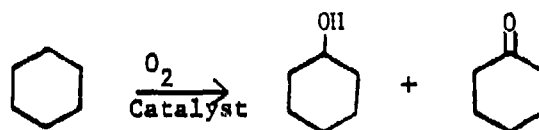


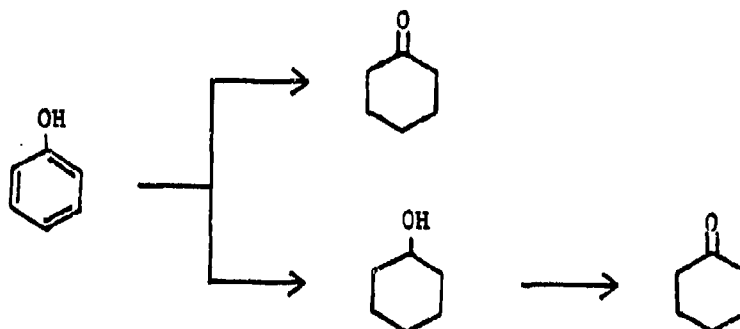
Figure III-3. Production of Cyclohexanone by the Air Oxidation Process (Lowenheim *et al.*, 1975).

This procedure yields a mixture of cyclohexanol and cyclohexanone.



Cyclohexane is oxidized in the presence of air at temperatures between 120 to 250°C. High pressure must be maintained to prevent vaporization of cyclohexane. Various catalysts such as metaboric acid may be used depending on the desired alcohol/ketone ratio. The oxidation product is hydrolyzed and separated from the catalyst and unreacted cyclohexane. If pure cyclohexanone is desired, the mixture can be dehydrogenated over a zinc oxide catalyst. The yield is between 90 and 95%.

The second process, catalytic hydrogenation of phenol, is shown schematically in Figure III-4. This process can either be accomplished in a one-step reduction directly to cyclohexanone or a two-step process with initial hydrogenation to cyclohexanol followed by dehydrogenation.



Phenol is reacted with hydrogen at temperatures from 100 to 200°C and pressures between 15 and 50 psi in the presence of a catalyst. Reduction can occur in either the liquid or vapor phase. A hydrogen/nitrogen gas mixture may be used also. If cyclohexanone is the desired product a palladium on carbon catalyst is used. A nickel catalyst yields cyclohexanol. The yield is reported as 95% (Lanké *et al.*, 1976; Lowenheim and Moran, 1975).

2. Manufacture, Production and Capacity

Production figures for cyclohexanone from 1965 to the present are given in Table III-5. Current manufacturers, cyclohexanone capacities, and production locations are presented in Table III-6. In 1977, El Paso Products discontinued their use and production of cyclohexanone, closing down a 6.5 million lb per year plant. Rohm and Haas, former producers of cyclohexanone, no longer manufacture it. Dow Badische, Monsanto, and Nipro manufacture cyclohexanone

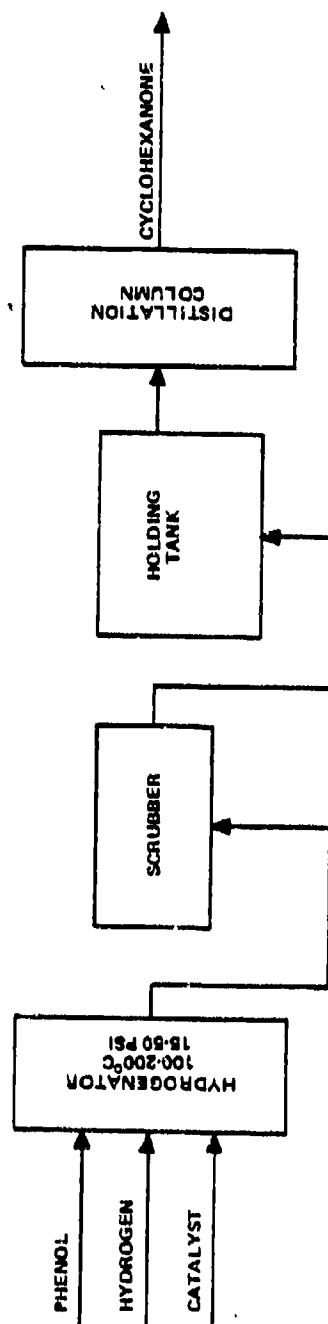


Figure III-4. Production of Cyclohexanone by Hydrogenation of Phenol (Lowenheim *et al.*, 1975).

Table III-5. U.S. Cyclohexanone Production, 1965 to present
(in million pounds) (U.S. Tarriff Commission).

<u>1965</u>	<u>1966</u>	<u>1967</u>	<u>1968</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>
322	314	430	482	704	715	756	783	683	651	554		

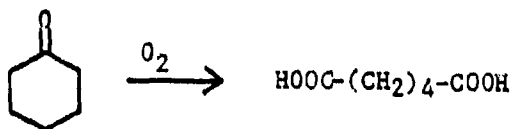
Table III-6. Current Producers of Cyclohexanone (Personal Communication).

<u>Manufacturer and Location</u>	<u>Process Used</u>	<u>Capacity (10⁶ lb/yr)</u>
Allied Chemical, Hopewell, VA	phenol, H ₂	420
Calanese Corp., Bay City, TX	cyclohexane, O ₂	100
Dow Badische, Freeport, TX	cyclohexane, O ₂	350
Monsanto, Pensacola, FL; Luling, LA	cyclohexane, O ₂	525
Nipro/nc., Augusta, GA	cyclohexane, O ₂	150
Union Carbide, Taft, LA	phenol, H ₂	45
	Total	1590

primarily for captive use as an intermediate for nylon. Allied Chemical and Union Carbide manufacture cyclohexanone for both sales and captive use. Allied Chemical manufactures chemical intermediates for nylon. Union Carbide uses cyclohexanone as a chemical intermediate in polycaprolactone plastics.

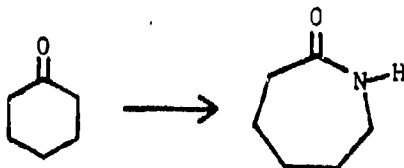
3. Usages

Cyclohexanone is primarily used as a chemical intermediate in the nylon industry. Oxidation of cyclohexanone cleaves the ring to yield adipic acid, a precursor of nylon-66.

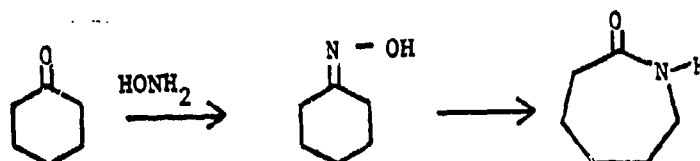


Mixtures of cyclohexanol and cyclohexanone can be oxidized to adipic acid circumventing the need for separation of the products from cyclohexane oxidation.

Also of major significance to the nylon industry is the transformation of cyclohexanone to caprolactam, used for the manufacture of nylon-6

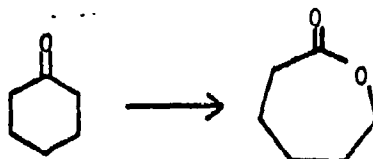


Hydroxylamine sulfate reacts with cyclohexanone to produce cyclohexanone oxime. The oxime readily transforms to caprolactam via a Beckman rearrangement.



Manufacture of adipic acid and caprolactam, respectively, account for 55% and 40% of the cyclohexanone used in the U.S.

Union Carbide oxidizes cyclohexanone under mild conditions to produce caprolactone, a cyclic ester.



The ester is polymerized to produce high impact plastics which are used in automobile bodies and skateboards. Caprolactone production is a minor use of cyclohexanone, limited to the 2.5% of the U.S. cyclohexanone production capacity possessed by Union Carbide.

Cyclohexanone is also employed as an industrial solvent for degreasing leather, cleaning metals, for ink, pesticides, paint and spot removers, RDX recrystallization and engine oil sludge.

4. Future Trends

In the early seventies, an increase in solvent usage of cyclohexanone was predicted due to the expected proliferation of regulations similar to L.A. Rule 66. Rule 66 classified many widely used ketonic solvents as photochemically reactive while classifying cyclohexanone as unreactive. To date substitution of cyclohexanone for more reactive solvents has not occurred to the extent that had been anticipated.

The nylon market which accounts for the great majority of cyclohexanone produced is healthy. In recent years there has been concern that as the nylon market grows there will be a shortage of cyclohexane (Greek, 1975). This shortage has not materialized and is now not expected to in the near future.

5. Documented or Speculated Occurrences in the Environment

Patterson *et al.* (1976) estimated 1974 total cyclohexanone emission to the air at 51.3 million pounds. The major source of these

emissions was the use of cyclohexanone as a solvent. They assumed that all cyclohexanone used as solvent would be vented to the environment upon evaporation. Emissions resulting from the manufacturing process were estimated at 1% of production by analogy to similar processes. Emissions occurring during bulk storage were estimated at 0.3 million pounds.

SOURCES AND EMISSION ESTIMATES OF CYCLOHEXANONE IN 1974
(Patterson *et al.*, 1976)

Source	Million pounds
Solvent Usage	42.5
Production Losses	8.5
Storage	0.3
Total	51.3

Although solvent use accounts for the largest amounts of cyclohexanone emissions, these sources tend to be small and geographically scattered. Sites of cyclohexanone production should have significantly larger emission densities. Average 24-hour ground level concentrations of cyclohexanone near production plants have been estimated at about 1.0 ppm (Patterson *et al.*, 1976).

Dow Badische estimates a yearly loss of six hundred thousand pounds of cyclohexanone based on a 0.002 pound loss per pound produced. These losses occur from reactor and tank vents, waste water streams, and as fugitive emissions (Dow Badische, 1978).

F. Comparison of Civilian and Military Usages and Pollution of Cyclohexanone

At current capacity, HAAP is a very minor user of cyclohexanone. Even at full mobilization, only 2,100,000 lb/yr of cyclohexanone would be used at HAAP. This usage represents only ~ 0.38% of 1975 U. S. production.

Only air emissions statistics of cyclohexanone from civilian production and usage were available. The civilian air emissions are estimated to be ~ 51.3 million lb. Thus, HAAP's total air and water effluents of cyclohexanone (a maximum of 2,100,000 lb/yr at full mobilization) represent only 4% of the civilian air emissions.

G. Environmental and Toxicological Hazards of Cyclohexanone

1. Human Exposure Studies

In a study of 353 workers exposed to cyclohexanone and other chemicals associated with caprolactam production, Pestrii (1970) found 114 workers

with non-specific autonomic nervous system disorders. Bernard *et al.* (1962) identified vascular, cellular and degenerative changes in the lungs and liver tissues of persons exposed to cyclohexanone. Skin contact causes defatting due to the solvent action of cyclohexane.

Several controlled exposure experiments have also been performed with human subjects. Nelson *et al.* (1943) exposed human subjects to cyclohexanone vapors. They reported eye irritation at 50 ppm. Exposure to 75 ppm was objectionable. The highest bearable concentration for an 8-hour day was 25 ppm.

Dobrinski (1966) studied the effect of cyclohexanone vapors on human brain activity. He determined the threshold limit for effects of cyclohexanone for rhythm reinforcement with the electroencephalogram. This threshold concentration was 22.4 ppb. The threshold concentration for conditioned reflex was 14.9 ppb. Dobrinski also determined the olfactory threshold to be 53.2 ppb. On the basis of the information gathered during the study, Dobrinski (1966) suggested a maximum permissible concentration for a single exposure of 9.9 ppb.

2. Mammalian Toxicity

a. Acute and Chronic Toxicity

Cyclohexanone is a common solvent. The toxicological properties of this compound have thus been relatively extensively investigated. A summary of the acute effects of cyclohexanone administration to mammals is presented in Table III-7. The data indicate that cyclohexanone is moderately toxic via all routes of administration.

Sublethal doses of cyclohexanone cause profound narcosis accompanied by central nervous system depression. Koeferl *et al.* (1976) observed sublethal effects of cyclohexanone in rats, dogs and monkeys. They found erythroid hyperplases and extramedullary hematopoiesis in the spleen of the dog.

Chronic exposure by both oral and inhalation routes also lead to central nervous depression. A summary of the chronic studies is presented in Table III-8.

b. Teratogenicity, Mutagenicity and Carcinogenicity

The teratogenicity of cyclohexanone was tested on chick embryos. Griggs *et al.* (1971) exposed eggs both prior to and after incubation for 96 hours. Chicks hatched from eggs exposed before incubation were normal, however, there was a higher rate of mortality compared to the controls. Chicks hatched from post-incubation exposed eggs developed locomotor difficulties and were unable to walk.

This preliminary evidence indicates that cyclohexanone may seriously affect the embryo. However, further studies are necessary to determine the dangers to the embryo.

Table III-7. Acute Toxicity of Cyclohexanone to Mammals.

Dilution and Vehicle	Route of Administration	Organism	Number Treated per Dose Level	Dose (g/kg)	Mortality Data	Reference
undiluted	oral	Rats, M,W (3-4)	5	1.541 (1.14-2.08)	14 day LD50 (± 1.96 S.D.)	Nycum et al., 1967
n.s.	oral	Rats, F	n.s.	1.34	14 day LD50	" "
undiluted	oral	Mice	n.s.	1.4	LD50	Novogordova et al., 1967
undiluted	oral	Rabbits, "young"	3	1.6-1.9	LD100	Treon et al., 1943
n.s.	oral	Mice		2.78	24 hr LD50	Caujolle & Caujolle, 1965
undiluted	i.p.	Mice		1.35	24 hr LD50	Caujolle et al., 1962
undiluted	i.p.	Guinea pig		0.76	8-40 hrs. min. lethal dose	Carasa & Gruziole, 1954
undiluted	i.v.	Dog		0.63	lethal dose	Caujolle & Roux, 1954
air	inhalation	Rats, Carworth-Wistar 4-5 wks 90-120 g	6	2000ppm (4) for 4 hrs.	1/6, anaesthesia after 4-6 hrs.	Nycum et al., 1967
			6	4000ppm (4) for 4 hrs.	6/6 anaesthesia after 1-5 hrs.	Nycum et al., 1967
			6	2131-3268 ppm	LC50 2639 ppm (± 1.96 S.D.)	Nycum et al., 1967
air	inhalation	Rats, Carworth-Wistar 4-5 wks 9-120 g	6	Sat. vap for 0.5 hrs.	0/6	"
			6	Sat. vap > 0.5 hrs.	Some deaths	"
			6	Sat. vap		
air	inhalation	Guinea pigs, F mixed stock 400-600 g	10	400 ppm (V/V) for 7.6 hrs.	3/10 died 4 hrs after exposure	Specht et al., 1940
undiluted	dermal 1 day std. cuff	Rabbit	4	0.948 (0.596-1.54)	14 day LD50 (± 1.96 S.C.)	Nycum et al., 1967
undiluted	dermal 5 ml at 20 ml intervals then wash < 4 hrs total exposure	Rabbit	n.s.	10.2-23.0	lethal range	Treon et al., 1943

Table III-8. Chronic Toxicity of Cyclohexanone.

<u>Animal</u>	<u>Administration</u>	<u>Dose (mg/kg/day)</u>	<u>Duration (days)</u>	<u>Mortality</u>	<u>Details</u>	<u>Reference</u>
Rats, M	Oral	0.01	180	no deaths	no effect noted	Novogorodova et al., 1967
		0.05	180	no deaths	slight changes in conditioned reflex activity	
		5.0	180	no deaths	marked changes in conditioned reflex activity; degenerative morphological changes of nervous system, liver, stomach, and spleen. (see text for details)	
Mice	Oral	280	25	no deaths	no changes in weight gain and general condition decline in work capacity on 25th day	"

<u>Animal</u>	<u>Conc. (ppm, v/v)</u>	<u>Hr/Day</u>	<u>Duration in days</u>	<u>Mortality</u>	<u>Details</u>	<u>Reference</u>
Rabbits, young, 4 per exposure group	182	6	70 (50 exposures, 5 days/wk x 10 wks)	no deaths	No signs of toxicity	Treon et al., 1943
	514	6	"	no deaths	Slight conjunctival congestion	
	1139	6	21 (15 exposures, 5 days/wk x 10 wks)	no deaths	Lethargy, slight salivation and lacrimation, conjunctival congestion	
	1822	6	"	no deaths	Lethargy, salivation, lacrimation, conjunctival congestion and irritation	

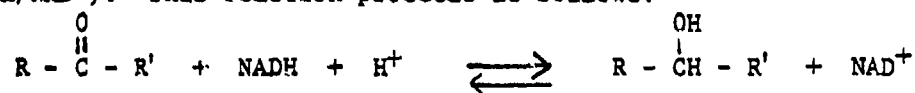
No information was uncovered on the mutagenicity or carcinogenicity of cyclohexanone. However, cyclohexanone has tentatively been selected for further testing (NCI, 1978).

c. Biochemistry of Cyclohexanone

Ketones can undergo a variety of reactions *in vivo*. These reactions include

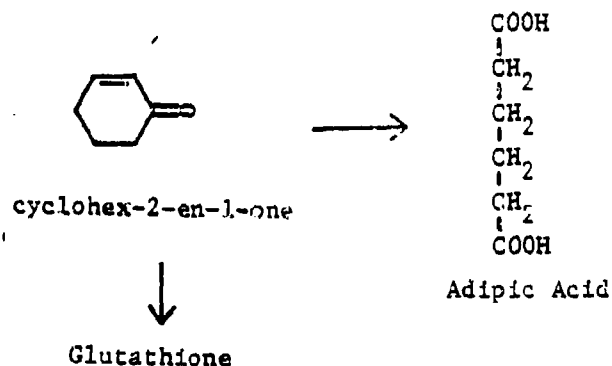
- reduction
- oxidation
- conjugation

Reduction reactions require the presence of nicotinamide adenine dinucleotide (NADH/NAD⁺). This reaction proceeds as follows:



In vivo studies on mammals indicate that 51-80% of the cyclohexanone is reduced to cyclohexanol (Elliott *et al.*, 1959).

Adipic acid has been found present in small amounts in the urine after intraperitoneal injection of cyclohexanone in mice (Filippi, 1914) and guinea pigs (Frey, 1939). Boyland and Chasseaud (1970) speculate the following oxidation reactions, which are based upon conversion of cyclohexanone *in vivo* to cyclohex-2-en-1-one:



Cyclohexanone is conjugated primarily as the glucuronide of cyclohexanol (Elliot *et al.*, 1959). Thus the ketone is first reduced to the alcohol. Some of the cyclohexanone can also be eliminated as the sulfuric acid ester. Ireon *et al.* (1943) followed the glucuronic acid and inorganic sulfate concentration in the urine of rabbits after oral administration of cyclohexanone. The results of their study are presented in Table III-9. The inorganic sulfates are decreased and the glucuronides increased. Similar studies by Deichmann and Dierker (1946) indicate that cyclohexanone is rapidly removed from the blood while urinary excretion occurs over a longer period of

time. Thus reduction to the alcohol and conjugation appears to be the main biochemical pathway for elimination of cyclohexanone. It does not appear in the urine as the free ketone.

Table III-9. Excretion of Glucuronic Acids and Sulfates in 24 Hour Urine Samples of Rabbits Following Oral Administration of Cyclohexanone (Treon *et al.*, 1943).

<u>Days After Dose</u>	<u>% Inorganic Sulfates</u>	<u>Glucuronic Acid (mg)</u>
[Dose]		
890 mg/kg (1)		
1	38.4	858
2	30.8	2,632
3	71.1	76
4	92.7	81
890 mg/kg (1)		
1	58.3	2,133
2	62.5	1,090
3	90.1	78
4	89.2	49
947 mg/kg (2)		
1	60	1,246
2	75	100
3	80	30

(1) Normal Daily Excretion of Glucuronic Acid in Rabbits, $35.2 \text{ mg} \pm 24.8$ [S.D.]

(2) Normal % Urinary Sulfates As Inorganic Sulfates, Approximately 85%

3. Aquatic Toxicity

Very few studies have been conducted concerning the levels and toxicity of cyclohexanone in aquatic systems. The acute toxicity levels of cyclohexanone to aquatic organisms are shown in Table III-10. From the fragmentary data, it appears that cyclohexanone has a very low toxicity to aquatic organisms. The high solubility of cyclohexanone in water (150 g/l at 10°C) indicates that the low toxicity is not related to the availability of the substance to the organisms.

Cyclohexanone is released in the HAAP G and H-Building waste water discharges. In an HAAP survey of the G and H-Buildings, approximately 109 lb/line of cyclohexanone were found to be released from the dewatering and composition B incorporation steps (USAEHA, 1971). Weekly grab samples for January through June, 1973, confirm the building survey results. During this 6-month period four lines were in operation. Two outfalls (B02A and B02B) were

Table III-10. Acute Toxicity of Cyclohexanone to Aquatic Organisms.

Species	Temperature °C	LC50 ppm 48 hour	Lethality ppm		Reference
			Level	Hours	
Rainbow trout	16-21	-	757	24	Lysak & Marcinek, 1972
<i>Salmo gairdneri</i>	16-21	-	303	24	"
"	13	-	5	24	Applegate et al., 1957
Bluegill	13	-	5	24	"
<i>Lepomis macrochirus</i>					
Sea Lamprey larvae	13	-	5	24	"
<i>Petromyzon marinus</i>					
Water flea	-	763	-	-	Warner et al., 1978
<i>Daphnia magna</i>					
Fathead minnow	-	<1350	-	-	"
<i>Pimephales promelas</i>					
Green sunfish	-	1100 (96 hr)	-	-	"
<i>Lepomis cyanellus</i>					

monitored. Cyclohexanone levels averaged 19 and 10 mg/l at these outfalls. Flow rates were estimated at 1.17 mgd and 3.62 mgd, respectively. The resulting discharge would be 487 lb of cyclohexanone. This number is in good agreement with the line figure of 109 lb/day. Assuming full mixing in the Holston River, the average river concentration would be only 0.03 ppm.

At maximum production 618 to 1616 lb/day of cyclohexanone could be discharged depending on the explosives being compounded. The Holston River concentration could be between 0.04 and 0.10 ppm. Even at 10 times these concentrations, cyclohexanone would not present a toxicity problem to aquatic organisms present in the Holston River. Table III-11 shows cyclohexanone levels in the Holston River at various degrees of mixing.

Table III-11. Cyclohexanone Levels in the Holston River (ppm).

Release at Full Mobilization
(Average flow 2070 million gallons per day)

Degree of Mixing	Cyclohexanone Used in the Incorporation Step	No Cyclohexanone Used in the Incorporation Step
1%	10.0	4.0
10%	1.0	0.4
100%	.1	.04

However, Helton (1978) found several compounds in the effluent of HAAP that are produced from cyclohexanone. Some of the compounds detected are 2-(1-cyclohexenyl)-cyclohexanone, 2-cyclohexylidenecyclohexanone, 2-cyclohexylcyclohex-2-enone, and several spiro compounds. The effects of these substances on aquatic organisms have not been evaluated.

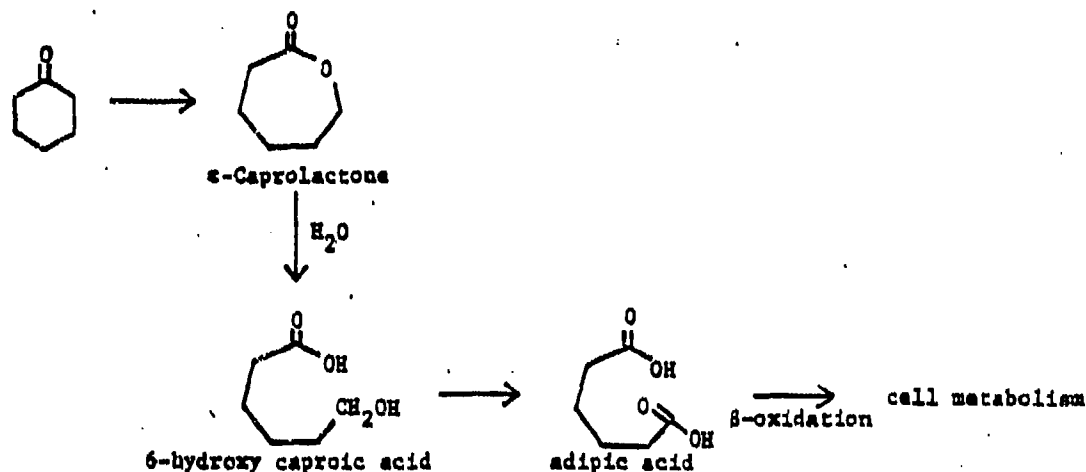
4. Phytotoxicity

No phytotoxic reactions were observed in specimens of bean, corn, cotton, cucumber, tobacco and tomato exposed to a 5% solution of cyclohexanone applied as a spray to foliage or liquid to roots (Gast & Early, 1956). No other information has been encountered.

5. Toxicity to Microorganisms

When cyclohexanone is used as the sole carbon source, growth inhibitions of certain microorganisms is observed. Terrestrial *Pseudomonas* sp. (Konovaltschihoff-Mazoyer and Senez, 1956) and several species of yeasts show no growth. However, Tanaka *et al.* (1977) have isolated a *Pseudomonas* bacteria which is capable of using cyclohexanone as the sole carbon source. Zussman *et al.* (1969) found no inhibition of growth of *Trichophyton rubrum* grown on cyclohexanone media.

A detailed study of the oxidation of cyclohexanone by *Nocardia globarula* was performed by Norris and Trudgill (1971). They proposed the following pathway for cyclohexanone oxidation by this bacterium.

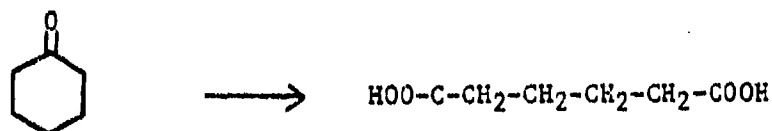


Thus cyclohexanone can be efficiently degraded by certain microorganisms even though it is inhibitory to others.

6. Environmental Fate

Due to its solubility in water, cyclohexanone discharged to the atmosphere will be washed down with rain. There is the possibility of atmospheric photolytic decomposition to carbon monoxide and pentene. This prediction is based on laboratory photochemistry (see Section C.2). Cyclohexanone solubilized in environmental waters can also undergo photolytic cleavage to hexanoic acid, analogous to its behaviour under laboratory conditions (see Section C.2).

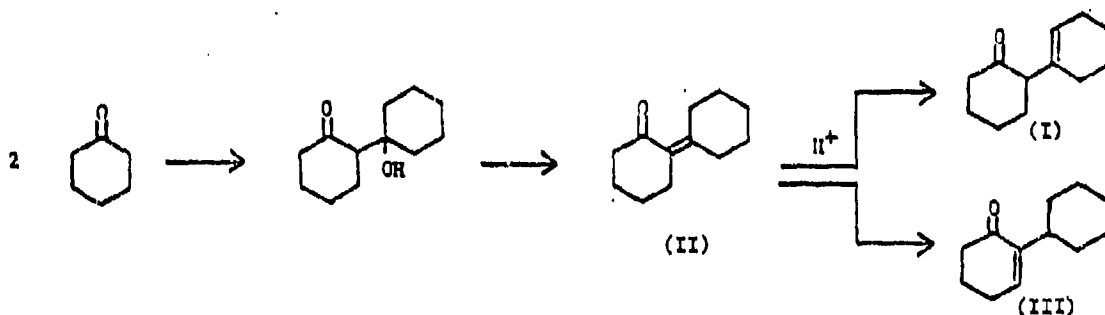
Studies have shown that cyclohexanone is metabolized to adipic acid by several pure strains of microorganisms (Lande *et al.*, 1976).



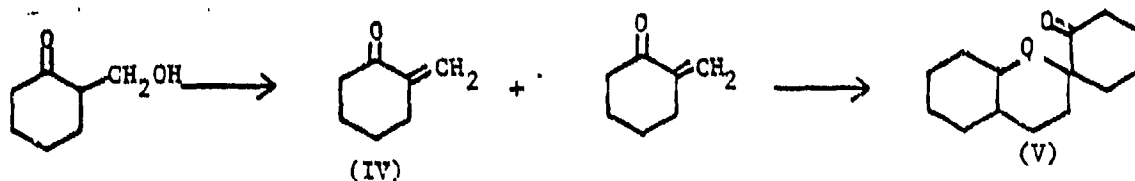
This degradation pathway is probably predominant in waters with high biological activity.

There is evidence (Helton, 1978) that the cyclohexanone waste from Holston AAP undergoes a variety of chemical transformations prior to environmental discharge. The major constituent in a chloroform extract of Building

H-2 wastewater was 2-hydroxymethyl-cyclohexanone. This compound is formed by an aldol type condensation of cyclohexanone and formaldehyde (see Section C.1). Three other components of the extract, 2-(cyclohexenyl)cyclohexanone (I), 2-cyclohexylidene-cyclohexanone (II), and 2-cyclohexyl-2-cyclohexenone (III), are products of an aldol type condensation between two molecules of cyclohexanone. Hydroxycyclohexenyl-cyclohexanone is initially formed. Dehydration is followed by rearrangements of the double bond.



Numerous minor compounds were observed in the chloroform extract. One has been identified as spiro [1-oxocyclohexane-2,2'-3',4',5',6',7',8'-hexahydrobenzo[(b)] pyran] (V). This compound is formed by the Diels-Alder addition of two molecules of 2-methylene cyclohexanone (IV), the dehydration product of 2-hydroxymethyl-cyclohexanone.



The structural identity of (V) has been confirmed by synthesis (personal communication with D.O. Helton). Identification of the other minor components is currently being undertaken.

The environmental fate and toxicity of these cyclohexanone reaction compounds is unknown.

7. Literature Availability for Phase II

Cyclohexanone is a common solvent. Many environmental and toxicological studies are reported in the literature. Thus sufficient information should be available for a Phase II detailed evaluation of toxicological and environmental hazards.

H. Standards and Regulations

1. Air and Water Acts

Rule 66 of the Los Angeles Pollution Control District places limits on emissions from industrial solvents. This rule applies to organic solvents exposed to baking, heat curing, heat polymerization or flame control and photochemical solvents. Cyclohexanone is considered as non-photoreactive by this law and its emissions are not limited.

2. Occupational Standards

OSHA (1974) has established the following limits on cyclohexanone in the work place

- vapor or gas 50 ppm
- particulate 200 mg/m³

These numbers correspond to the published threshold limit values (TLV). The USSR has a considerably lower limit of 10 mg/m³ (Lande et al., 1976).

3. Department of Transportation

No hazard labels are required for shipment of cyclohexanone under the Code of Federal Regulations. However, cyclohexanone is listed on the U.S. Coast Guards' CHRIS list (1274).

I. Conclusion and Recommendations

The civilian and military uses and pollution of cyclohexanone and its toxicological and environmental hazards have been reviewed during this problem definition study. After evaluating the data, the following conclusions were drawn:

1. Cyclohexanone is not a military unique chemical as only 0.38% of the U.S. 1975 production would be used by HAAP at full mobilization; full mobilization pollution projection of the chemical would represent only 4% of the 1974 civilian air emissions.
2. Additional data on the carcinogenic and teratogenic potential of cyclohexanone are needed. However, carcinogenic and teratogenic bioassays on cyclohexanone itself should be a low Army priority.
3. The formation of cyclohexanone addition compounds in the Holston AAP effluent appears to be a military unique problem. It appears that the proposed biotreatment facility for HAAP will adequately remove cyclohexanone from the HAAP effluent.

In view of these findings, cyclohexanone itself should be a low priority

for a detailed Phase II toxicological evaluation, unless new experimental evidence uncovers further problems with this compound. However, the cyclohexanone addition products require further investigation. This investigation should incorporate the following:

- further sampling to quantitate the presence of these addition compounds
- a literature review of the reported chemical toxicological and environmental properties of these compounds
- mammalian and aquatic toxicological studies should be carried out on those compounds which are present in significant concentrations and for which sufficient literature data is not available.

J. References

- Andrew, P.; Smith, A.F. and Wood, R. (1971), "A Simple Field Test for Determination of Cyclohexanone and Methylcyclohexanone Vapours in Air," *Analyst*, 96, 528.
- Applegate, U.; Howell, J.; Hall, A. and Smith, M. (1957), "Toxicity of 4,346 Chemicals to Larval Lampreys and Fishes," U.S. Fish Wildlife Ser. Spec. Sci. Rep. Fisheries, No. 207.
- Bernard, B.; Pallade, S.; London, M.; Popovich, K.; Gol'dshtein, I.; Mikhail, G.; Mandrik, G. and Vancha, G. (1962), "Effect of Certain Toxic Substances Used in the Protection of Plastics on the Organism," *Pr. Toksikol. i Klinika Prof. Zabollevanii Khim. Etiol.* (Gos. Izd. Med. Lit.), 133.
- Boyland, E. and Chasseaud, L.F. (1970), "The Effect of Some Carbonyl Compounds on Rat Liver Glutathione Levels," *Biochem. Pharmacol.*, 19, 1526.
- Calvert, J. and Pitts, J. (1966), *Photochemistry*, John Wiley and Sons, New York.
- Caujolle, D. and Caujolle, F. (1965), "Toxicity Gradient of the Cycloalkanones," *Compt. Rend.*, 261(F), (Group 13), 1781.
- Caujolle, F.; Caujolle, D. and Foulquier, J.L. (1962), "Toxicity for the Mouse of Some Cyclanones," *Compt. Rend.*, 254, 2245.
- Caujolle, F. and Roux, G. (1954), "Sur la Toxicité Immédiate de la Carvomenthone, de la Carvone, de la Pipepéritone, et de la Pipepériténone," *Compt. Rend.*, 239, 680.
- Celanese Chemical Company, *Cyclohexanone*, Technical Data Document.
- Ceresa, C. and Gruziooli, C. (1951), "Experimental Cyclohexanone Intoxication," *Med. Lavomo*, 42, 253.
- Deichmann, W.B. and Dierker, M. (1946), "The Spectrophotometric Estimation of Hexuronates (Expressed as Glucuronic Acid) in Plasma or Serum," *J. Biol. Chem.*, 163, 753.
- Dobrinskii, A. (1966), "Cyclohexanol and Cyclohexanone in Atmospheric Air and Their Hygienic Significance," *Biol. Diastvie i Gigien Znachenie Atm Zagryazneni*, 119(32), from *Chem. Abstr.* 65:14324.
- Dow Badische (1978). Letter from W. P. Towland.
- Elliott, T.H.; Parke, D.V. and Williams, R.T. (1959), "Studies in Detoxication 79, The Metabolism of Cyclo[¹⁴C]hexane and its Derivatives," *Biochem. J.*, 72, 193.

- Filippi, E. (1914), "Physiological Action and Behavior of Some Derivatives of Benzene Compared to Those of Cyclohexane," *Arch. Pharmacol. Sper.*, 18, 178.
- Frey, J. (1939), "The Effect of Cyclohexanone Upon the Hematopoietic System," *Haematologica*, 20, 725, in Lande, S.S. *et al.*, 1976, "Investigation of Selected Potential Environmental Contaminants: Ketonic Solvents," NTIS, PB - 252-970.
- Gast, R. and Early, J. (1956), "Phytoxicity of Solvents and Emulsifiers Used in Insecticide Formulations," *Agr. Chem.*, 11(4) 42, 136.
- Greek, B.F. (1975), "Nylon Growth Will Tax Raw Materials Supply," *Chem. Eng. News*, October 20.
- Griggs, J.H.; Weller, E.M.; Palmisano, P.A. and Niedermeier, W. (1971), "The Effect of Noxious Vapors on Embryonic Chick Development," *Ala. J. Med. Sci.*, 8(3), 342.
- Hawley, G.C. (1977), *The Condensed Chemical Dictionary*, 9th Edition, Van Nostrand Reinhold Co., N.Y.
- Helton, D. (1978), "Subtask 9, Identification of Waste Products from RDX and HMX Manufacture," Monthly Report No. 16, U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD, Cont. # DAMD-17-74-C-4073.
- Kirk, R.E. and Othmer, D.F. (1967), *Encyclopedia of Chemical Technology*, Vol. 12, John Wiley & Sons, New York.
- Koeferl. M.T.; Port, C.D.; Garvin, R. and Dosner, J.L. (1976), "Subacute Toxicity of Cyclohexanone in Rats, Dogs and Monkeys "Abstracts: Fifteenth Annual Meeting, 45.
- Konovaltschihoff-Mazoyer, M. and Senez, R.D. (1956), "Dégradation Bactérienne des Hydrocarbures Paraffiniques," *Annales De L'Institut Pasteur*, 91, 60.
- Lande, S.S.; Durkin, P.R.; Christopher, D.H.; Howard, P.H. and Saxena, J. (1976), "Investigation of Selected Potential Environmental Contaminants: Ketonic Solvents," NTIS, PB - 252-970.
- Lowenheim, F.A. and Moran, M.K. (1975), *Faith, Keyes and Clark's Industrial Chemicals*, 4th edition, John Wiley and Sons, New York.
- Lysak, A. and Marcinek, J. (1972), "Multiple Toxic Effect of Simultaneous Action of Chemical Substances on Fish," *ROCZ., Nauk Roln. Ser.*, H 94, 53.
- March, J. (1968), *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, McGraw-Hill, New York.

- NCI (1978), "Chemicals Being Tested for Carcinogenicity by the Bioassay Program, DCCP, NCI," Feb., 1978.
- Nelson, K.; Ege, J.; Ross, M.; Woodman, L. and Silverman, L. (1943), "Sensory Response to Certain Industrial Solvent Vapors," *J. Ind. Hyg. Toxicol.*, 25, 282.
- Norris, D.B. and Trudgill, P.W. (1971), "Metabolism of Cyclohexanol by *Nocardia globetula* Cl 1," *Biochem. J.*, 121(3), 363.
- Novogorodova, L.; Savelova, V. and Sengear, A. (1967), "Experimental Basis for the Permissible Concentrations of Cyclohexanone in Reservoir Waters," *Pr. Zagryazneniya Vodoemov*, 8, 101, in Lande, S.S. et al., 1976, "Investigation of Selected Potential Environmental Contaminants: Ketonic Solvents," PB - 252-970.
- Nycum, J.; Condra, N. and Kinkpad, E. (1967), "Cyclohexanone Range Finding Toxicity Studies," Mellon Institute Special Report, 30, in Lande, S.S. et al., 1976, "Investigation of Selected Potential Environmental Contaminants: Ketonic Solvents," PB - 252-970.
- OSHA (1974), "Occupational Safety and Health Administrative Standards," *Federal Register*, 39(125), 23541.
- Parkes, D.G.; Ganz, C.R.; Polinsky, A. and Schulze, J. (1976), "A Simple Gas Chromatographic Method for the Analysis of Trace Organics in Ambient Air," *Amer. Ind. Hyg. Assoc. J.*, 165.
- Patterson, R.M.; Bornstain, M.I. and Garshick, E. (1976), "Assessment of Cyclohexanone as a Potential Air Pollution Problem," PB-258 359.
- Pestrii, N. (1970), "State of the Nervous System of Workers Producing Caprolactam," *Gig. Tr. Prof. Zabol.*, 14(6), 37.
- Pouchert, Charles J. (1970), *The Aldrich Library of Infrared Spectra*, Aldrich Chemical Co., Inc.
- ©Sadtler Research Laboratories, Inc. (1966), Sadtler Index, Philadelphia, Pa.
- Sax, N.I. (1976), *Dangerous Properties of Industrial Materials*, 4th edition, Van Nostrand Reinhold Co., N. Y.
- Specht, H.; Miller, J.; Valaer, P. and Sayers, R. (1940), "The Response of Guinea pigs to the Inhalation of Ketone Vapors," NIH Bull. No. 176, U.S. Pub. Hlth Serv., in Lande, S.S. et al., 1976, "Investigation of Selected Potential Environmental Contaminants: Ketonic Solvents," PB - 252-970.
- Srinivasan, R. (1963), "Photochemistry of the Cyclic Ketones," in Noyes, W.A.; Hammond, G. and Pitts, J. (1963), *Advances in Photochemistry, Volume 2*, Interscience Publishers, New York.

- Tanaka, H.; Shikata, K.; Obata, H.; Tokuyanna, T. and Ueno, T. (1977), "Isolation and Cultural Conditions of Cyclohexanone-Utilizing Bacterium," *Hakko Kogaku Kaishi*, 55(2), 57.
- Treon, J.; Crutchfield, W. and Kitzmiller, K. (1943), "The Physiological Response of Rabbits to Cyclohexanone, Methyl Cyclohexanone, and Certain Derivatives of these Compounds. I. Oral Administration and Cutaneous Application," *J. Ind. Hyg. Toxicol.*, 25(6), 199.
- USAEHA (1971), "Waste Flow Characterization, Area B, Holston Army Ammunition Plant, Kingsport, Tennessee," Letter Report and Attachments.
- U.S. Coast Guard (1974), *Chemical Hazards Response Information System*, CG-446-2.
- Wallace, T.; Pobiner, H. and Schriesheim, A. (1965), "Solvent Effects in the Base-Catalysed Oxidation of Ketones to Mono- and Dicarboxylic Acid," *J. Org. Chem.*, 30, 3768.
- Warner, M.; Randall, W.F.; Diehl, S.A.; Pearson, J.G. and Meier, E.P. (1978), "Acute Toxicity of Several Munitions Related Compounds to *Daphnia Magna*, Fathead Minnows and Green Sunfish," Draft, U.S. Army Research and Development Laboratory, Technical Report.
- Weast, R.C. (1975), *Handbook of Chemistry and Physics*, 56th edition, CRC Press, Ohio.
- Windholz, M. (1976), *The Merck Index*, 9th edition, Merck and Co., Inc., Rahway, N.J.
- Zussman, R.; Vicher, E. and Lyon, I. (1969), "Incorporation of Acetate Into *Trichophyton Rubrum* Phenylalanine," *Mycopathol. Mycol. Appl.*, 37(1), 86.

AD

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

METHYLAMINES

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1973

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

METHYLAMINES

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAND17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

SUMMARY

The methylamines are by-products of the RDX/HMX manufacture at Holston Army Ammunition Plant. The main documented source of entry of these compounds into the environment is from the Building A-1 still sludge. At present mobilization levels, this still operates only one week out of every four months. However, at full mobilization, the still would operate continuously. When in operation, the effluent from this still is discharged into Arnett Branch which flows directly into the Holston River. This discharge is ~21,000 gallons per day containing ~3500 mg/l methylamine, ~2200 mg/l dimethylamine and ~180 mg/l trimethylamine. Discharges from the acid recovery operations enter Arnett Branch in the same vicinity. Thus the unique situation of high nitrate and high dimethylamine concentrations exist in this Branch. This situation may lead to the formation of N-nitrosodimethylamine under favorable conditions of low pH or high microbial activity.

The A-1 still is the only source of entry of the methylamines into the environment from Holston Area B operations that has been documented. However, the possibility exists of discharge of the methylamine salts from the acids removal and wash operations in Building E.

The civilian uses of the methylamines are numerous and widespread. Current production capacity is about 323 million lb/year of mono-, di- and trimethylamine in the equilibrium ratio. Trimethylamine is used almost exclusively as a chemical precursor for choline chloride. The major uses of dimethylamine are for the production of dimethylformamide and dimethylacetamide. Monomethylamine is used as an intermediate in the synthesis of insecticides and surfactants. It is the most widely used of the methylamines.

The methylamines are widespread through the ecosystem being present in fish, plants, food, etc. They are not toxic to mammals, fish, microorganisms, plants, etc. in small amounts. In most organisms, biochemical pathways exist for converting small amounts of the methylamines to CO₂ and ammonia or into cellular material. Even in acute doses, they are relatively non-toxic with an LD50 > 100 mg/kg for mammals and a 48 hr LC50 > 300 mg/l for fathead minnows. The invertebrates appear to be more sensitive to these compounds than the other organisms tested with a 48 hour LC50 of 32 mg/l for trimethylamine.

Once present in the environment, there are several species of microorganisms which can efficiently degrade the methylamines. However, the possibility of N-nitrosodimethylamine formation in the environment exists. The formation of this highly potent carcinogen is favored when high concentrations of dimethyl- or trimethylamine and nitrite or nitrate are present in a low pH or high microbial environment. Once formed, this compound may persist long enough to reach drinking or recreational water.

The methylamines are not a unique military problem. They are wide spread throughout the ecosystem. However, the discharges from the A-1 still Holston AAP are a significant load on the local aquatic system. In addition, the presence of a high nitrate content in the same effluent can lead to the

formation of the highly toxic N-nitrosodimethylamine. This potential nitrosamine formation requires further evaluation. It is, therefore, recommended that a detailed evaluation of the environmental fate of the methylamines be carried out in Phase II. This evaluation should be backed-up with sampling and analysis data from Holston. Additional sampling should also be conducted to determine if any methylamines or their derivatives are discharged from the E-Buildings. A detailed evaluation of the toxicological hazards of the methylamines in Phase II should be a low priority.

FOREWORD

This report details the results of a preliminary problem definition study on the methylamines. The purpose of this study was to determine the Army's responsibility for conducting further research on the methylamines in order to determine their toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on the methylamines, the military and civilian usage and pollution of these chemicals were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

The methylamines were only three of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

TABLE OF CONTENTS

	Page
Summary	IV-3
Foreword	IV-5
A. Introduction	IV-9
B. Alternate Names	IV-9
C. Physical Properties	IV-10
D. Chemical Properties	IV-10
1. General Reactions	IV-10
2. Environmental Reactions	IV-15
a. N-nitrosodimethylamine	IV-15
b. Photochemical Decomposition	IV-20
c. Oxidation Reactions	IV-21
3. Sampling and Analysis	IV-21
E. Uses in Army Munitions Production	IV-23
1. Purposes	IV-23
2. Estimated or Speculated Occurrences in the Environment	IV-24
F. Uses in Civilian Community	IV-24
1. Production Methodology	IV-24
2. Production, Manufacture and Capacities	IV-26
3. Usages	IV-27
4. Future Trends	IV-28
5. Documented or Speculated Occurrences in the Environment	IV-28
G. Comparison of Military and Civilian Usage and Pollution . .	IV-30
H. Toxicological and Environmental Hazards	IV-30
1. Toxicity to Mammals	IV-30
2. Aquatic Toxicity	IV-33
3. Degradation of the Methylamines by Microorganisms . . .	IV-34
a. Biochemical Pathways for Microbial Degradation of the Methylamines to Formaldehyde and Ammonia .	IV-34
b. Formation of N-nitrosodimethylamine by Micro- organisms	IV-36
4. Phototoxicity	IV-39
5. Availability of Literature for Phase II	IV-43
I. Regulations and Standards	IV-43
1. Air and Water Standards	IV-43
2. Occupational Exposure Limits	IV-43
3. Department of Transportation	IV-44
J. Conclusions and Recommendations	IV-44
K. References	IV-47

NO PAGE MARKING

LIST OF TABLES

<u>Number</u>		<u>Page</u>
1	Physical Properties of Methylamine, Dimethylamine and Trimethylamine	IV-11
2	Yields of N-nitrosodimethylamine at 100°C and at Different pH Values.	IV-16
3	Formation of N-nitrosodimethylamine from Trimethylamine or Trimethylamine Oxide and Nitrite in Acetic Acid.	IV-17
4	Amounts of N-nitrosodimethylamine Formed From Equimolar Amounts of Dimethylamine and Trimethylamine	IV-18
5	Amount of N-nitrosodimethylamine Formed From Equimolar Amounts of Trimethylamine and Dimethylamine at Different Acidities and Temperatures	IV-19
6	Levels of the Methylamines in Arnott Branch as a Function of Different Degrees of Mixing	IV-24
7	U.S. Producers of Methylamines	IV-26
8	Uses of Methylamines	IV-28
9	Dimethylamine in Foodstuffs and Tobacco	IV-29
10	Acute Toxicity of the Methylamines to Mammals	IV-31
11	Acute Toxicity of the Methylamines to Aquatic Organisms	IV-33
12	N-nitrosodimethylamine Production by Various Bacteria	IV-37
13	Quantity and Quality of Effluents Which May be Discharged from the Manufacture of the Methylamines	IV-42

LIST OF FIGURES

1	Infrared Spectra of the Methylamines	IV-12
2	Ultra-violet Spectra of the Methylamines	IV-13
3	Nucleophilic Addition Reactions of the Methylamines.	IV-14
4	Oxidative Degradation Reactions of the Methylamines.	IV-22
5	Production of the Methylamines	IV-25
6	<i>In vivo</i> Metabolic Scheme for the Methylamines	IV-32
7	Oxidation of Trimethylamine by Obligate and Facultative Methylotrophs.	IV-35
8	The Oxidation of N-methyl Compounds to Formaldehyde.	IV-37
9	N-nitrosodimethylamine Formation in Sewage	IV-40
10	Formation of N-nitrosodimethylamine in Samples of Lake Water of Differing Acidities	IV-41
11	Formation of N-nitrosodimethylamine in Sterile and Nonsterile Langford Soil.	IV-42

IV. THE METHYLAMINES

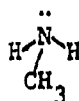
A. Introduction

The methylamines are unintentional by-products of the manufacture of RDX and HMX at Holston AAP. Due to their similar chemical behavior and their common points of entry into the environment from both the Civilian and Military Sectors, the three methylamines will be discussed together.

B. Alternate Names

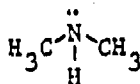
Methyl-, dimethyl- and trimethylamine are aliphatic amines which result from the successive replacement of hydrogen on ammonia by methyl groups. The structure of the methylamines and pertinent alternate names are listed below:

Methylamine



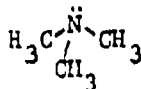
Molecular Weight:	31.06 g/mole
CAS Registry No.:	74-89-5
CA Name (9CI):	Methanamine
CA Name (8CI):	Methylamine
Wiswesser Line Notation:	Z1
Synonyms:	Aminomethane; Carbinamine; Monomethylamine

Dimethylamine



Molecular Weight:	45.08 g/mole
CAS Registry No.:	124-40-3
Replaces CAS Registry No.:	14534-15-7
CA Name (9CI):	Methanamine, N-methyl-
CA Name (8CI):	Dimethylamine
Wiswesser Line Notation:	IM1

Trimethylamine



Molecular Weight:	59.11 g/mole
CAS Registry No.:	75-50-3
CA Name (9CI):	Methanamine, N,N-dimethyl-
CA Name (8CI):	Trimethylamine
Wiswesser Line Notation:	1N1

C. Physical Properties

The physical properties of the methylamines are presented in Table IV-1. The infrared spectra and the ultraviolet spectra of the methylamines are shown in Figures IV-1 and IV-2.

D. Chemical Properties

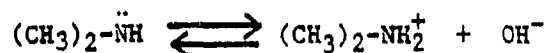
1. General Reactions

The chemistry of the methylamines is centered on nitrogen's unshared electron pair. These unbonded electrons account for the predominant chemical properties of the methylamines: their basicity and their nucleophilic behavior.

Basicity constants for the methylamines are (Morrison and Boyd, 1973):

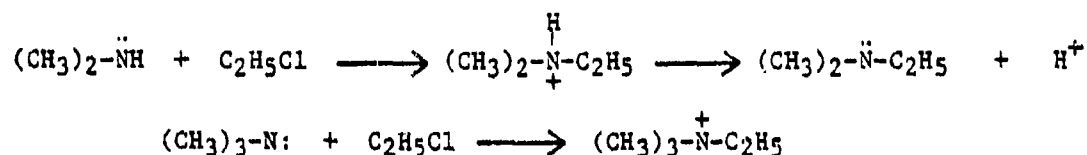
	K_b
monomethylamine:	4.5×10^{-4}
dimethylamine:	5.4×10^{-4}
trimethylamine:	0.6×10^{-4}

Under strongly alkaline conditions, the methylamines exist in solution as the free base. At pH 10, the



ratio of free amine to protonated ammonium ion is approximately one. At a pH 4, essentially all the amine exists in the ionic form.

Mono and dimethylamine are excellent nucleophiles, participating in a wide number of additions and substitution reactions. Trimethylamine is a less effective nucleophile. The bulkiness of the third methyl substituent sterically hinders nucleophilic attack. Additionally, lack of an amine proton prevents relief of the positive charge from the addition product.



Several well known reactions involving the methylamines as nucleophiles are compiled in Figure IV-3.

Both di- and trimethylamine in nitrous acid form N-nitrosodimethylamine, a reaction which will be discussed in the next section. The reaction of monomethylamine with HNO_2 does not produce a nitrosamine but results in diazotization.

Table IV-1. Physical Properties of Methylamine, Dimethylamine and Trimethylamine.*

	<u>Methylamine</u>	<u>Dimethylamine</u>	<u>Trimethylamine</u>
Physical Form @ 20°C:	gas	gas	gas
Color:	colorless	colorless	colorless
Odor:	strong ammoniacal	ammoniacal or dead fish	ammoniacal; fishy
Odorfactory Threshold:	53 ppm	53 ppm	<100 ppm
M.P.:	-92.5°C	-92.2°C	-117.3°C
B.P.:	-6.3°C @ 760 mmHg -19.7°C @ 400 mmHg -32.4°C @ 200 mmHg -43.7°C @ 100 mmHg -73.8°C @ 10 mmHg	6.88°C @ 760 mmHg	2.87°C @ 760 mmHg
Vapor Pressure:	1396 mmHg @ 20°C 2600 mmHg @ 25°C 5170 mmHg @ 52°C	1260 mmHg @ 20°C	340 mmHg @ 25°C
Critical Pressure:	73.6 atm	52.4 atm	40.2 atm
Critical Temperature:	156.9°C	164.6°C	160.2°C
Liquid Density:	0.6624g/ml @ 20°C 0.6560g/ml @ 25°C 0.6114g/ml @ 60°C	0.6556g/ml @ 20°C 0.6496g/ml @ 25°C 0.6046g/ml @ 60°C	0.6331g/ml @ 20°C 0.6271g/ml @ 25°C 0.5828g/ml @ 60°C
Vapor Density at 760 mmHg:	1.396g/l @ 0°C	1.966g/l @ 17°C	2.580g/l @ 17°C
Heat of Vaporization at Boiling Point:	6.17 Kcal/mole	6.33 Kcal/mole	5.48 Kcal/mole
Heat of Combustion of Gas:	259 Kcal/mole	422 Kcal/mole	586 Kcal/mole
Autoignition Temperature in air:	430°C	402°C	190°C
Flash Point:			
Explosive Limits in Air:	4.95 - 20.75% vol.	2.80 - 14.40% vol.	2.00 - 11.60% vol.
Solubility:			
water at 1 atm	42.5% wt.	60.0% wt.	20.0% wt.
ethanol at 1 atm, 20°C	400/cc/lcc	727/cc/lcc	600/cc/lcc
methanol at 1 atm, 20°C	656/cc/lcc	992/cc/lcc	573/cc/lcc
nitrobenzene at 1 atm, 20°C	88/cc/lcc	226/cc/lcc	154/cc/lcc
	also soluble in ether and aromatic hydrocarbon		

*References: Commercial Solvents Corporation, 1965; Windholz, 1976; Department of Transportation, 1974; Sax, 1976; Hawley, 1977.

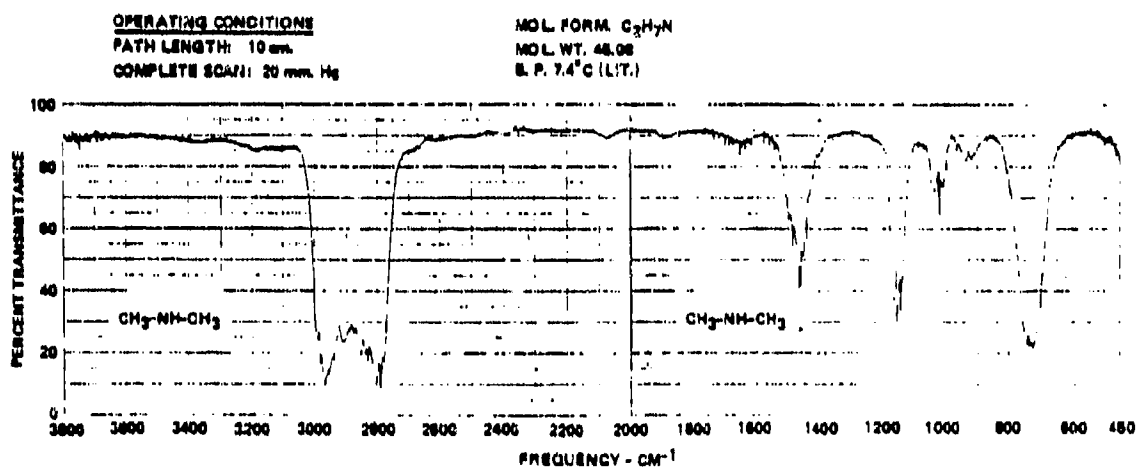
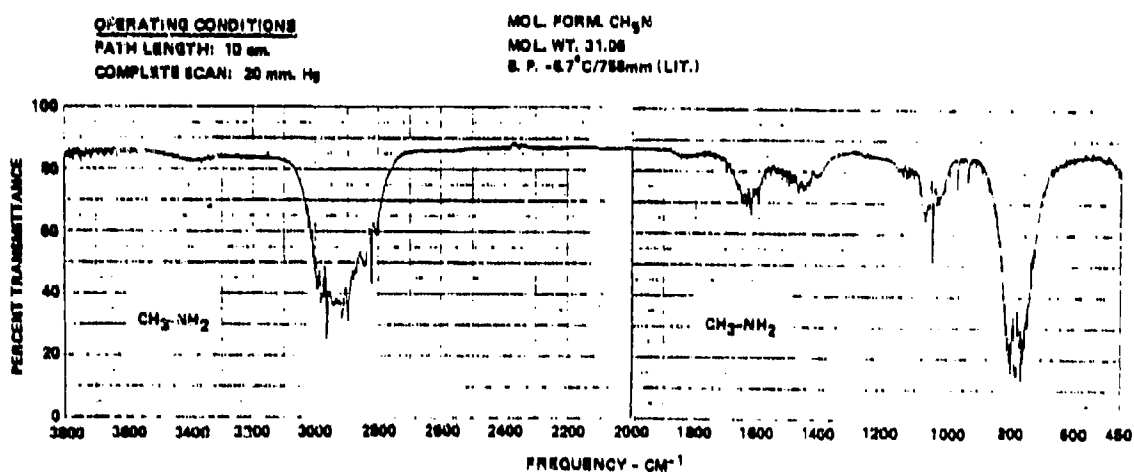
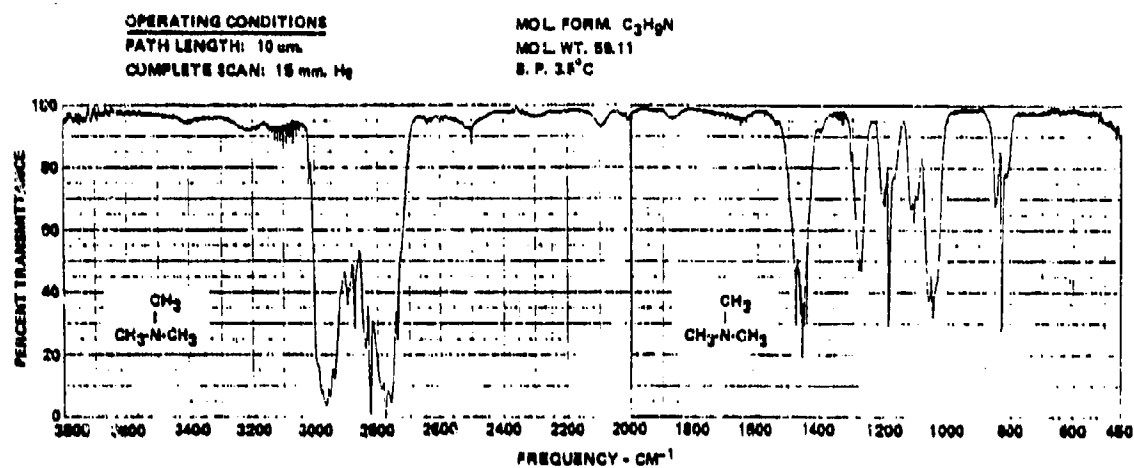
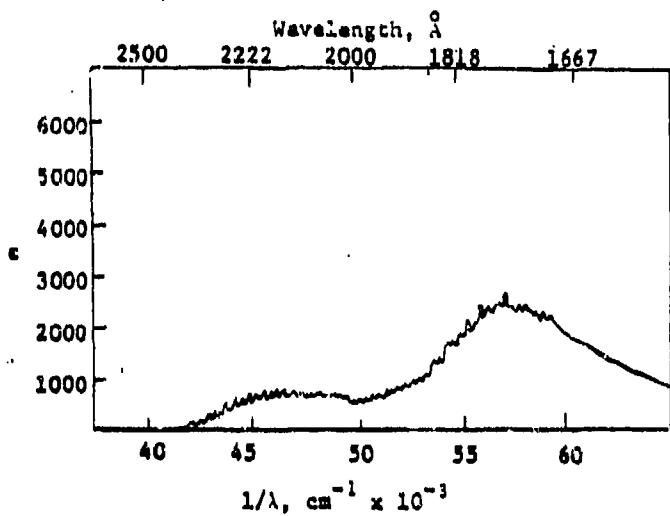


Figure IV-1. Infrared Spectra of the Methylamines
(Pouchert, 1975).



Ultraviolet Spectrum of Dimethylamine

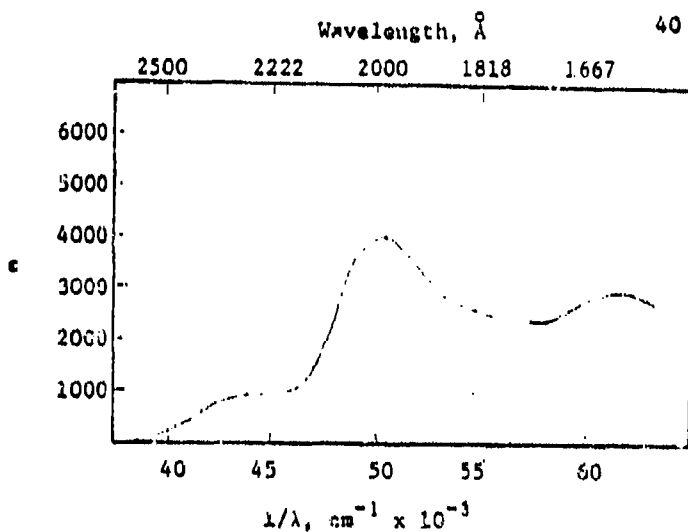
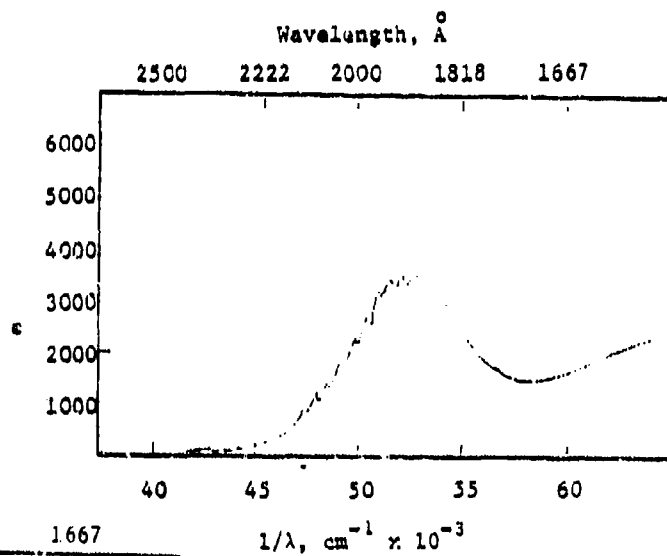
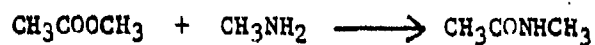


Figure IV-2. Ultraviolet Spectra of the Methylamines (Calvert and Pitts, 1967).

1. Mannich Reaction:



2. Amide Formation:



3. α , β Aminoalcohol Formation:



4. Dithiocarbamate Formation:

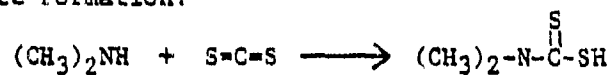
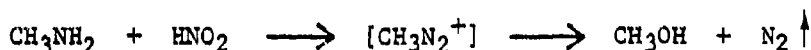
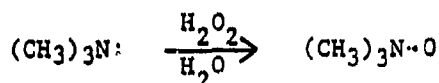


Figure IV-3. Nucleophilic Addition Reactions of the Methylamines.
(March, 1968; Commercial Solvents, 1965)

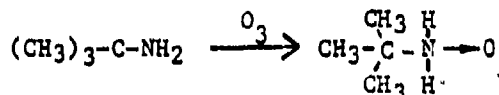


Unlike their aromatic analogs, aliphatic diazo compounds are unstable and decompose spontaneously. In water, diazomethane decomposes to methanol and molecular nitrogen.

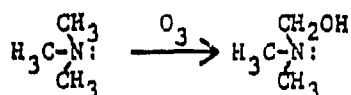
Methylamines can be oxidized with aqueous hydrogen peroxide to amine oxides.



Oxidation of alkylamines with ozone can occur along two pathways. Amine oxide formation can occur and is the predominant reaction in ozonation of tert-butylamine.



The methylamines possess primary alkyl substituents and undergo side chain oxidation in competition with oxide formation.

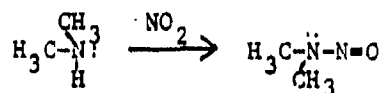


Side chain oxidation to N,N-dimethylcarbinolamine is predominant in trimethylamine ozonation (Evans, 1975).

2. Environmental Reactions

a. N-nitrosodimethylamine Formation

Currently the environmental transformation of methylamines to N-nitrosodimethylamine is of major concern. It can be formed from dimethylamine, trimethylamine, or trimethylamine oxide. Tables IV-2 through IV-5 summarize some of the experimental results. Nitrosation of dimethylamine occurs readily in solution.



The reaction has been carried out at a variety of temperature and pH's. Mildly acidic conditions are most favorable with N-nitrosodimethylamine formation from nitrous acid and dimethylamine optimized at pH 5. At the extremes of pH, values less than 2 and larger than 10, nitrosation does not occur. N-nitrosodimethylamine is not formed to an appreciable extent in basic environments (pH 7 to 9) in the absence of a catalyst. In the presence of

Table IV-2. Yields of N-nitrosodimethylamine at 100°C and at Different pH Values^a (Lijinsky and Singer, 1974).

pH	NDMA formed (Z yield) ^b					
	Dimethylamine	Dimethylamine + Formaldehyde ^c	Trimethylamine	Trimethylamine + Formaldehyde ^c	Trimethylamine oxide	Trimethylamine Oxide + Formaldehyde ^c
1	2	3	3	3	44	72
3	62	58	2	3	15	22
3.5	77	—	8	—	—	—
4	87	—	25	—	—	—
4.5	93	—	14	—	—	—
5	106	93	9	9	3	3
7	2	56	9	5	0.1	1
9	2	31	—	—	—	—
11	0	1	—	—	—	—

^a 0.05 M amine + 0.25 M sodium nitrite in perchloric acid

^b After 4 hours

^c 0.05 M formaldehyde

Table IV-3. Formation of N-nitrosodimethylamine from Trimethylamine or Trimethylamine Oxide and Nitrite in Acetic Acid (pH 3.7-4.0) at 90°C (Lijinsky and Singer, 1973).

Concentration of Nitrite	NDMA formed (% yield) ^a	
	0.5 M Trimethylamine	0.5 M Trimethylamine Oxide
5 M	57	54
4 M	54	58
3 M	44	48
2 M	41	40
1.5 M	40	35
1 M	31	20
0.75 M	23	9
0.5 M	11	4
0.25 M	5	0.2
0.2 M	0.05 M Trimethylamine	0.05 M Trimethylamine Oxide
	15	19
0.04 M	0.01 M Trimethylamine	0.01 M Trimethylamine Oxide
	1.3	20

^aAfter 4 hours.

Table IV-4. Amount of N-nitrosodimethylamine Formed from Equimolar Amounts of Dimethylamine and Trimethylamine (Scanlan *et al.*, 1974).

mmol of amine/ 100 ml	Molar ratio amine: nitrite	NDMA formed, ppm ^a	NDMA from DMA divided by NDMA from TMA
0.58 DMA	1:1	0.540	8.1
0.58 TMA	1:1	0.066	
4.44 DMA	7.6:1	12.9	2.3
4.44 TMA	7.6:1	5.6	
17.8 DMA	30.4:1	64.9	1.3
17.8 TMA	30.4:1	51.1	
44.4 DMA	76:1	133.5	0.64
44.4 TMA	76:1	208.9	
88.8 DMA	152:1	233.5	0.60
88.8 TMA	152:1	388.7	

Conditions: pH 6.4, 100° for 2.5 hr., NaNO₂, 0.58 mmol/100 ml (400 ppm)

^appm in the reaction solution

Table IV-5. Amount of N-nitrosodimethylamine Formed From Equimolar Amounts of Trimethylamine and Dimethylamine at Different Acidities and Temperatures (Scanlan *et al.*, 1974).

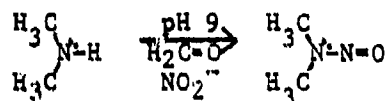
pH	Temperature °C	NDMA from DMA, ppm ^a	NDMA from TMA, ppm ^a
6.4	100	37.1	3.61
6.4	24	0.5	0.010
3.2	37	8.6	0.209

Concentrations: amines, 4.44 mmol/100 ml
NaNO₂, 2.22 mmol/100 ml.

Reaction time: 2.5 hr.

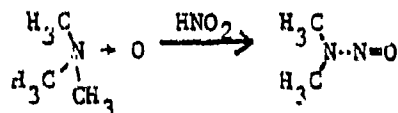
^appm in the reaction solution

formaldehyde, which acts as an electrophilic catalyst, dimethylamine will undergo extensive nitrosation even under basic conditions (Roller and Keefer, 1973).

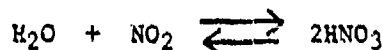


Trimethylamine will react with HNO_2 to form N-nitrosodimethylamine. At ratios of amine to nitrite ranging from one to ten, this reaction is several times slower than nitrosamine formation from dimethylamine. As the amine to nitrite ratio increases, the rates of N-nitrosodimethylamine formation from the two amines is comparable. At amine to nitrite ratios of 152 to 1, trimethylamine conversion is faster. Optimum pH for the reaction at 100°C is 3.2 (Scanlan *et al.*, 1974).

Trimethylamine oxide in HNO_2 also leads to formation of N-nitrosodimethylamine (Lijinsky and Singer, 1973).



N-nitrosodimethylamine formation has been observed from dimethylamine vapor and atmospheric HNO_2 (Hanst *et al.*, 1977).



Nitrosation of dimethylamine vapor occurs following the rate equation (Hanst *et al.*, 1977).

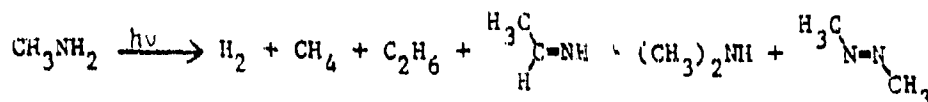
$$\frac{d(\text{CH}_3)_2\text{NNO}}{dt} = k \cdot P_{\text{HNO}_2} \cdot P_{(\text{CH}_3)_2\text{NH}} \quad k=0.08 \text{ ppm}^{-1} \text{ min}^{-1}$$

Photolytic decomposition of HNO_2 occurs much more rapidly than its formation. For this reason atmospheric N-nitrosodimethylamine will form only at night.

N-nitrosodimethylamine also undergoes photolytic decomposition to nitric oxide, carbon monoxide, formaldehyde and an unidentified compound. Atmospheric half-lives of thirty and sixty minutes (a clear sunny day and a cloudy day) at 11:00 a.m. have been observed (Hanst *et al.*, 1977).

b. Photochemical Decomposition

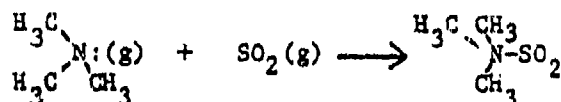
Photolysis of monomethylamine generates hydrogen, methane, ethane, ethylenimine, dimethylamine and azomethane (Terenin and Vilesov, 1963).



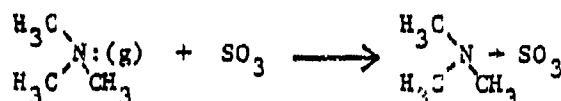
Primary processes involve hydrogen radical generation and homolytic cleavage of C-N bonds.

The photolysis of di- and trimethylamine should be similar. Photolytic decomposition of trimethylamine has been reported to yield ethane, hydrogen and methane suggesting the generation of methyl and hydrogen radicals. Nitrogen radicals will also be generated which might undergo various recombinations and/or oxidations.

Trimethylamine undergoes a non-photolytic gas phase reaction with SO₂ at ordinary temperature to form a solid (Burg, 1943).

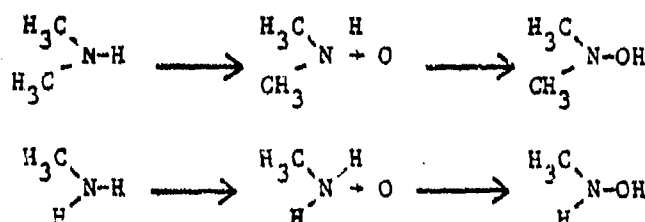


An amine:SO₃ adduct can also be formed



c. Oxidation Reactions

Oxidation of methylamines in water to either N-oxides or carbinolamines may result in eventual degradation to formaldehyde and ammonia. The reaction sequences are illustrated in Figure IV-4. N-oxidation of mono- and dimethylamine will lead to hydroxylamines.



3. Sampling and Analysis

Gas chromatography is the most useful analytical method for the methylamines. It has been applied to detection of methylamines in gas samples, in solution, and absorbed in tissues. A variety of columns, detectors, and conditions have been used by many investigators. GC procedures have been developed for the separation and determination of methylamines in the atmosphere (Okita, 1970), in biological fluids (Dunn *et al.*, 1976), in fish tissues (Gruger, 1972, Miller *et al.*, 1972), in various foodstuffs (Singer and Lijinsky, 1976), in plants (Khranova and Bokarev, 1976), and in wastewater (Onuska, 1972). Quantitative analysis at the µg/ml, µg/g and ppm levels have been widely reported. Lower limits of detection are on the order of ng/ml (ng/g, and ppb).

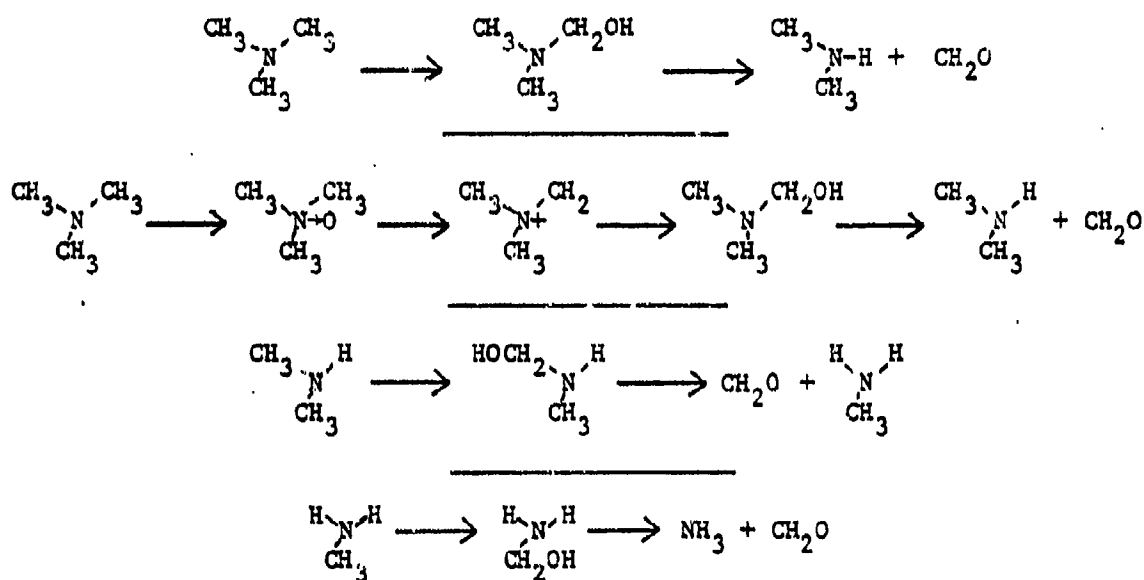


Figure IV-4. Oxidative Degradation Reactions of the Methylamines.

Other analytical techniques for methylamines include:

- Ion exchange chromatography has been used for the separation and determination of mono-, di-, and trimethylamine and ammonia in aqueous solutions. Reliable results were obtained with samples containing 150-450 ppm monomethylamine, 10-50 ppm dimethylamine, and 10-50 ppm trimethylamine (Bouyoucos, 1977).

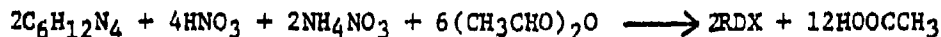
- Low temperature infrared spectroscopy was demonstrated to be applicable to the identification of amines in the air. This technique has limited use for quantitative estimations (Ball and Purnell, 1976).

- An automated method for routine determination of trimethylamine in fish was developed in the early sixties. Improvements on the method now allow determination of dimethylamine and ammonia as well. Analyses can be done on the µg/ml level at a rate of 30 samples per hour (Ruiter and Weseman, 1976).

E. Uses in Army Munitions Production

1. Purposes

The methylamines are not used or intentionally produced in the production of munitions. They are, however, produced in substantial quantities as by-products in the manufacture of RDX and HMX at Holston AAP. RDX is made by the Bachmann process which involves the nitration of hexamine according to the following reaction:

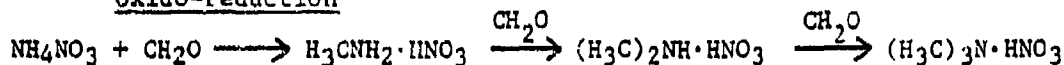


The Bachmann process uses a large amount of nitrate salts along with the nitric acid. In the reactor environment, hexamine can be partially degraded to ammonia and formaldehyde. The formaldehyde formed can undergo a variety of reactions including

Cannizino



Oxido-reduction



As discussed in Section II of this report (the hexamine report), the yields of RDX and HMX are only ~65% based on the hexamine used. The remainder of the hexamine ends up as impurities such as formaldehyde, formic acid, the methylamines, SEX and TAX. The exact amount of the individual methylamines formed is highly dependent on operating conditions. However, methylamine is always present in significantly greater quantities than dimethyl- or trimethylamine.

2. Estimated or Speculated Occurrences in the Environment

The A-1 Building still sludge is the main documented source of the entry of methylamines into the environment. Significant quantities of methylamine salts or derivatives could also enter the environment from the E Buildings. However, the quantities of methylamines discharged from the E Buildings have not been monitored.

At current production levels, the A-1 still operates one week every four months. At full mobilization this still would operate continuously. At a still feed rate of 15 gallons per minute, ~21,000 gallons per day are discharged into Arnett Branch (USAHA, 1971). This discharge contains ~3,500 mg/l methylamine, ~2,200 mg/l dimethylamine and ~180 mg/l trimethylamine plus other products such as hexamine, formaldehyde, ammonia and copper (Adams and Whiting, 1976). Therefore, 613 lb/day of methylamine, 385 lb/day of dimethylamine and 31.5 lb/day of trimethylamine would be discharged from this still. Thus, estimated concentrations of the methylamines in Arnett Branch (assuming full mixing and a Branch flow rate of 21 million gallons per day) are 3.5, 2.2 and 0.2 mg/l of methylamine, dimethylamine and trimethylamine, respectively. However, full mixing would not be expected to occur immediately. Therefore, local concentration could be very high as indicated below.

Table IV-6. Estimated Levels of the Methylamines in Arnett Branch as a Function of Different Degrees of Mixing.

Degree of Mixing	Concentration in mg/l		
	Methylamine	Dimethylamine	Trimethylamine
1%	350	220	18
10%	35	22	1.8
100%	3.5	2.2	0.2

In addition to the potentially high dimethylamine content in Arnett Branch, this water also contains large amounts of nitrates from Area B acid recovery operations. Thus, the potential exists for formation of N-nitrosodimethylamine.

F. Uses in Civilian Community

1. Production Methodology

Mono-, di-, and trimethylamine are produced together in a continuous process by the reaction of ammonia and methanol. Figure IV-5 shows the process schematically. Anhydrous ammonia and methanol are fed continuously to a vaporizer. The resulting gas stream flows through the heat exchanger and a super-heater to the reaction vessel packed with an amination catalyst. The ammonia and methanol react exothermically to form a mixture of methylamines.

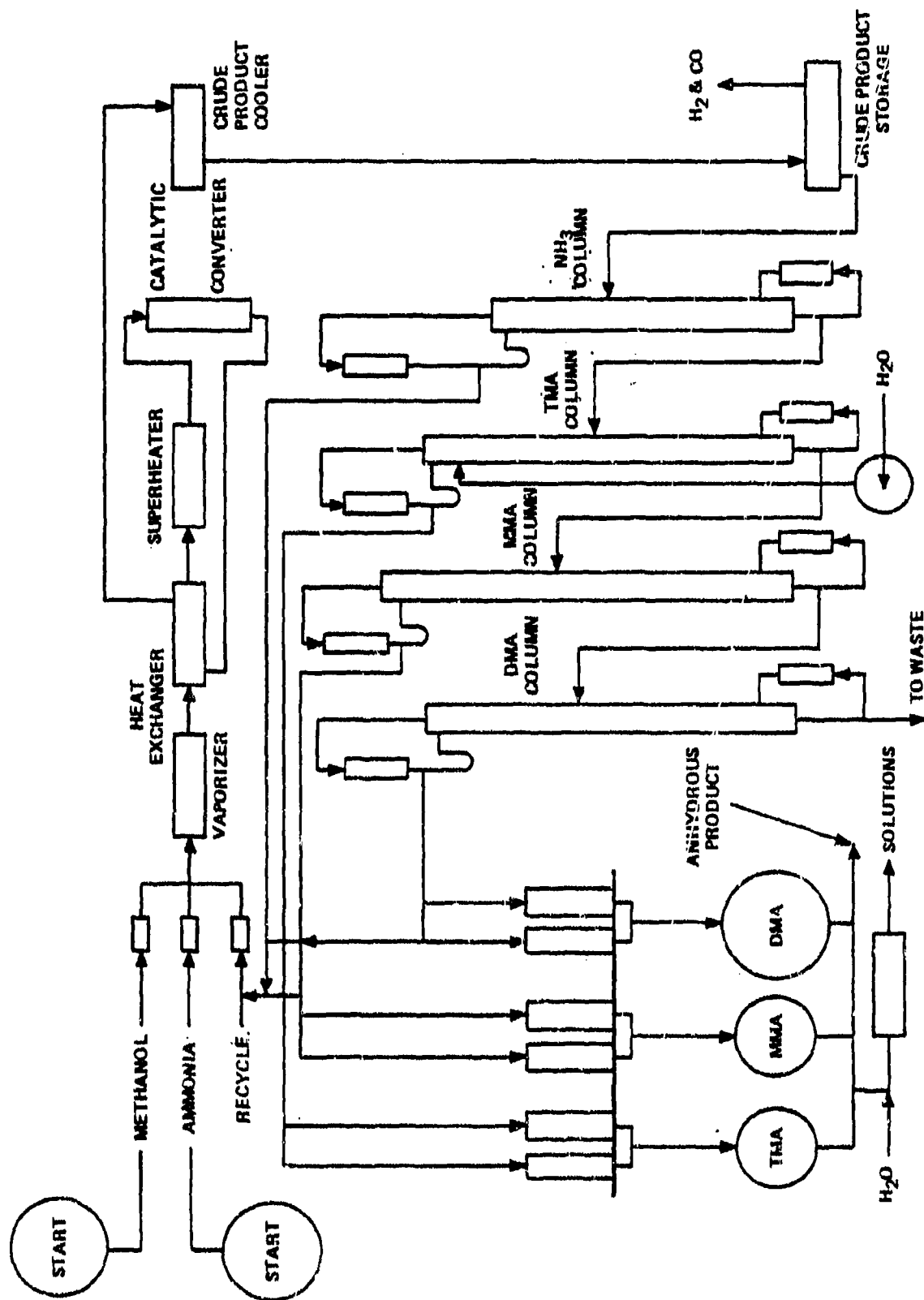


Figure IV-5. Production of the Methylamines.

The hot gaseous products are passed through the heat exchanger where heat is exchanged with the forward gas flow. The gaseous methylamines then go to a condenser where the crude product liquifies prior to separation.

The crude product containing ammonia, water and the three methylamines is fed to a series of four distillation columns. The first column removes the excess ammonia as a trimethylamine: ammonia azeotrope. This mixture is recycled. The bottoms are fed to the second column where pure trimethylamine is removed via extractive distillation. The bottoms from the second column are fed to the third column where monomethylamine is obtained as top product steam. Dimethylamine is distilled off the top of the fourth column. The remaining water is drained to waste. The yields are 95% from ammonia and methanol. Product purity is better than 99% (Leonard Process Co., Inc., 1978).

The crude product mixture is an equilibrium system with the ratio of mono- to di- to trimethylamine fixed by the reactor parameters. If a particular methylamine is desired in larger proportions, the other two may be recycled to the reactor to suppress new formation of their species. This allows flexibility to accommodate variations in the market.

2. Production, Manufacturers, and Capacities

Production capacities and sites are in Table IV-7.

Table IV-7. U.S. Producers of Methylamines (S.R.I., 1977a).

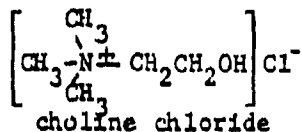
Producers	Capacities 10 ⁶ lb/yr
Air Products and Chemicals, Pensacola, Florida	100
E.I. duPont, Belle, West Virginia La Porte, Texas	185
GAF Corporation, Calvert City, Kentucky	10
IMC Chemical Group, Terre Haute, Indiana	28
Total	323

The capacities are for mono-, di-, and trimethylamine in the equilibrium ratio. If the products are recycled to increase the amount of a desired amine, the capacities are significantly lower (S.R.I., 1977a).

The Pennwalt Corporation and Rohm and Haas currently have methylamine plants on standby with respective capacities of 10 million and 14 million pounds per year.

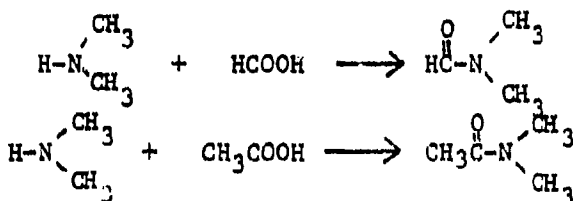
3. Usages

Trimethylamine is used almost exclusively as a chemical precursor for choline salts.

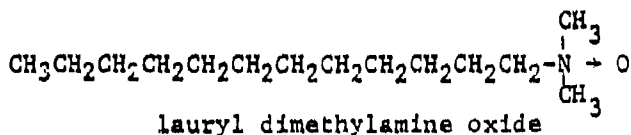


Numerous choline salts are used as therapeutic and nutritional agents

Dimethylamine has a wide variety of applications. Production of dimethylformamide and dimethylacetamide accounts for fifty percent of dimethylamine consumption.



Dimethylformamide and dimethylacetamide are used as solvents in the acrylic fiber and butadiene industry. The manufacture of lauryl dimethylamine oxide, a surfactant, is the second major use of dimethylamine.

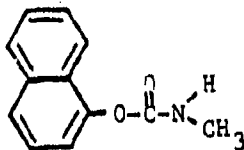


The third major use of dimethylamine is the synthesis of rubber accelerators. These include thiurams and metal salts of dimethyldithiocarbamic acid.



Miscellaneous uses of dimethylamine include the amine salt of the herbicide 2,4-D, as an intermediate for unsymmetrical dimethylhydrazine for rocket fuels and in the dye, drug and leather industry.

Monomethylamine is used as an intermediate for 1-naphthyl-N-methylcarbanate, a contact insecticide.



Other uses of monomethylamine include starting materials for the synthesis of surfactants, methylhydrazine, methyl nitrate, and methyl pyrrolidone.

The uses of methylamine are tabulated below.

Table IV-8. Use of Methylamines (Lowenheim, 1975; S.R.I., 1977b).

Use	% Consumed
Monomethylamine	
Insecticides	50
Surfactants	25
Other	25
Dimethylamine	
Dimethylformamide/Dimethylacetamide	50
Lauryl dimethylamine oxide	15
Rubber Accelerators	15
Other	20
Trimethylamine	
Choline Compounds	95
Other	5

4. Future Trends

The versatility of the methylamines for use as intermediates has allowed good growth for these chemicals. Future growth rates of 7-8% per year are expected. However, this growth is highly dependent on the agricultural chemical market. This market could be adversely affected by the Toxic Substances Control Act. If the 7-8% predicted growth rate is realized, new production capacities will be needed by the early 1980's (Chem. Week, 1977).

5. Documented or Speculated Occurrences in the Environment

Methylamines have been identified in flowers, plants, and trees (Smith, 1971). Amine producing flowers are generally characterized by a fishy smell. Trimethylamine occurs in *Chamopodium vulvaria*, a plant which smells strongly of fish. Methylamine and trimethylamine have been detected in apple spurs. Methylamine and dimethylamine along with other aliphatic amines have been identified in the air around cattle feedyards (Mosier *et al.*, 1973).

Dimethylamine and trimethylamine are known to be present in commercial fish. Large quantities can be generated during storage and significant research has gone into the detection of amines in marine fish (Gruger, 1972).

Singer and Lifjnsky (1976) have investigated a variety of consumer goods for secondary amines and found dimethylamine present in canned tuna, frozen and fresh fish, ham, hot dogs, milk, coffee, tea, beer, wine, and tobacco. Their findings are tabulated in Table IV-9.

Table IV-9. Dimethylamines in Foodstuffs and Tobacco

	<u>μmol/100g</u>	<u>ppm</u>
Canned tuna	51	23
Frozen ocean perch	400	180
Frozen cod	1640	740
Freshwater trout	15	7
Freshwater bass	250	110
Salmon	180	82
Baked ham	5	2
Hot dogs	2	1
Evaporated milk	7	3
Whole milk	0.8	0.2
Coffee	4	2
Tea	1.6	0.7
Canned beer	1.3	0.6
Bottled beer	1.6	0.7
Wine	0.2	0.07
Tobacco	-	9-75
<u>Cigarette smoke (condensate)</u>	1.8 ^a	110
^a μg per cigarette		

G. Comparison of Military and Civilian Usage and Pollution

The methylamines are produced in large volumes by the civilian community. Current production capacity is 323 million lb/yr of mono-, di- and trimethylamine in the equilibrium ratio. In addition, the methylamines are wide spread throughout the ecosystem. The Army does not intentionally manufacture methylamines. They are, however, by-products of RDX/HMX manufacture at HAAP. The methylamines enter the environment in significant quantities when the Building A-1 still is in operation. Thus, although the Army's discharge of methylamines is minor compared with that of the civilian production and use, it can be significant to the local ecosystem at HAAP. Due to the high nitrate concentration in HAAP discharges, the potential for N-nitrosodimethylamine formation exists. For this reason, the HAAP discharges of methylamines are relatively unique since high nitrate and dimethylamine concentrations are not normally located in the same area.

H. Toxicological and Environmental Hazards

1. Toxicity to Mammals

A summary of various acute toxicity studies with the methylamines is presented in Table IV-10. In general, the acute toxicity of the methylamines to mammals is fairly low with LD50's averaging several hundred mg/kg.

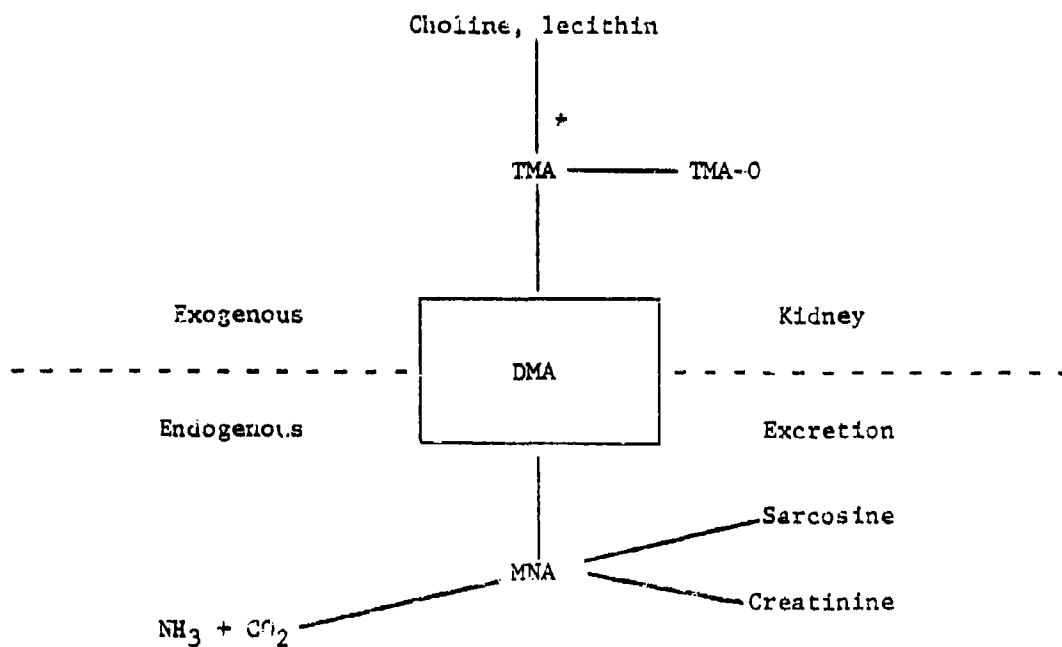
The main toxicological danger from the methylamines is due to the potential *in vivo* formation of N-nitrosodimethylamine. This toxic chemical has been shown to be a carcinogen in animals (NIOSH, 1977). This carcinogen is known to be readily formed under acidic conditions and high nitrite concentration. Methylamine and trimethylamine can also be metabolized to dimethylamine by the biochemical pathway shown in Figure IV-6.

Several researchers have investigated the potential *in vivo* formation of N-nitrosodimethylamine. For example, Ishiwata *et al.* (1975) showed N-nitrosodimethylamine could be produced from dimethylamine hydrochloride, sodium nitrate and glucose in the presence of human saliva. Lane and Bailey (1973) studied the formation of N-nitrosodimethylamine in human gastric juices. When 100 ppm each of nitrite and dimethylamine were present in the gastric juices, the optimum pH for N-nitrosodimethylamine formation was determined to be 2.5. Mirvish (1970) found a slightly higher optimum of pH of 3.4 for N-nitrosodimethylamine formation in gastric juices. The formation of N-nitrosodimethylamine under neutral anaerobic conditions in rat caecal intestine contents has also been shown to occur (Klubes and Jondorf, 1971). They hypothesized that the nitrosamine formation was dependent on metabolism by intestinal microorganisms.

Studies on the conversion of dimethylamine to N-nitrosodimethylamine have only found nitrosamine formation at very high levels of dimethylamine and nitrite. If it can be shown that N-nitrosodimethylamine is also formed at lower levels of dimethylamine, then the chronic toxicity of the methylamine to mammals and man will be a major problem which must be attacked in the future.

Table IV-10. Acute Toxicity of the Methylamines to Mammals.

Animal	Compound	Administered	Dose mg/kg	Effect	Reference
Mouse	Methylamine	s.c.	2500	LDLO	Stecher, 1968
Rat	Dimethylamine	Oral	698	LD50	Dzanashuili, 1967
Mouse	Dimethylamine	Oral	316	LD50	Dzanashuili, 1967
Rabbit	Dimethylamine	Oral	240	LD50	Dzanashuili, 1967
Guinea pig	Dimethylamine	Oral	240	LD50	Dzanashuili, 1967
Mouse	Trimethylamine	i.p.	75	LDLO	NIOSH, 1977
Mouse	Trimethylamine	i.v.	90	LD50	NIOSH, 1977
Mouse	Trimethylamine	s.c.	1000	LDLO	Bovet and Bovet-Nitti, 1948
Rabbit	Trimethylamine	s.c.	800	LDLO	NIOSH, 1977
Rabbit	Trimethylamine	i.v.	400	LDLO	Bovet and Bovet-Nitti, 1948



* = Bacterial action

TMA - trimethylamine

TMA-O - trimethylamine oxide

DMA - dimethylamine

MNA - monomethylamine

Figure IV-6. *In vivo* Metabolic Scheme for the Methylamines.
(Simenhoff, 1975)

2. Aquatic Toxicity

The methylamines are known to occur naturally in aquatic systems. For example, trimethylamine has been shown to be produced in fish (Sasajima, 1968) and algae (Sakevich, 1970). In spite of their wide spread occurrence in the ecosystem, the methylamines are relatively toxic to many aquatic organisms when presented in acute doses. Results of acute toxicity studies with *Daphnia magna* and the Fathead Minnow are summarized in Table IV-11.

Table IV-11. Acute Toxicity of the Methylamines to Aquatic Organisms.

Species	Substances	Hours	LC50	Reference
<i>Daphnia magna</i>	Methylamine	24	>125	Warner et al., 1973
" "	Methylamine	48	96.3	" "
" "	Dimethylamine	24	155	" "
" "	Dimethylamine	48	135	" "
" "	Trimethylamine	48	32-56	" "
Fathead Minnow (<i>Pimephales promelas</i>)	Methylamine	24	>320	" "
" "	Methylamine	48	>320	" "
" "	Methylamine	96	298	" "
" "	Dimethylamine	24	>560	" "
" "	Dimethylamine	48	>560	" "
" "	Dimethylamine	96	210	" "
" "	Trimethylamine	24	<560	" "
" "	Trimethylamine	48	<320	" "
" "	Trimethylamine	96	226	" "

Using creek chub (*Semotilus atromaculatus*) Gillette et al. (1952) found methylamine and dimethylamine were totally lethal over 24 hours exposure of 30 ppm and 50 ppm, respectively.

The HAAP A-1 Building still sludge is the main documented source of entry of the methylamines into the environment. As discussed in Section E of this report, the concentration in Arnott Branch could be as high as 350 mg/l for methylamine, 220 mg/l for dimethylamine and 18 mg/l for trimethylamine assuming 1% mixing. These levels and even levels at 10% mixing (see Table IV-6) would present a significant danger to aquatic organisms in the Branch.

In addition to the toxicity from the methylamines alone, the toxicity of the degradation products of these compounds must also be considered. As discussed in the following section, the methylamines can be degraded to formaldehyde and ammonia or under some circumstances form N-nitrosodimethylamine.

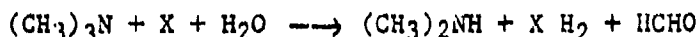
3. Degradation of the Methylamines by Microorganisms

a. Biochemical Pathways for Microbial Degradation of the Methylamines to Formaldehyde and Ammonia

Anthony (1975) has listed a number of microorganisms known to be methylotrophic or have the ability to grow on organic compounds containing no carbon-carbon bonds. N-methyl compounds such as trimethylamine, dimethylamine and methylamine have been shown to be degraded by bacteria including species of *Pseudomonas*, *Achromobacter*, *Acetobacter* and *Mycobacterium* (Grabinska-Loniewska, 1974).

The oxidation of tertiary, secondary, and primary amines by microorganisms is catalyzed by specific enzymes which are inducible. Each methyl group of an N-methyl compound is oxidized to one molecule of formaldehyde, which is then further oxidized through formic acid to CO₂ or assimilated into cell material by the ribulose monophosphate cycle or the serine pathway. This pathway is illustrated by Colby and Zatman (1973) in Figure IV-7.

There are two routes known for the oxidation of trimethylamine, the products in both cases being dimethylamine and formaldehyde. In certain obligate methylotrophs, organisms whose growth substrates are restricted to specific carbon compounds containing no carbon-carbon bonds, dimethylamine and formaldehyde are produced by an anaerobic oxidative demethylation catalysed by trimethylamine dehydrogenase. The reaction is as follows:

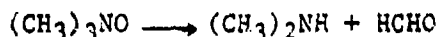


(where X = a natural hydrogen acceptor as yet undetermined)

In the facultative methylotrophs, organisms whose growth substrates include a variety of other organic compounds lacking carbon-carbon bonds, two enzymes and a reduced coenzyme are required. The first enzyme is a monooxygenase and the product is trimethylamine-N-oxide.



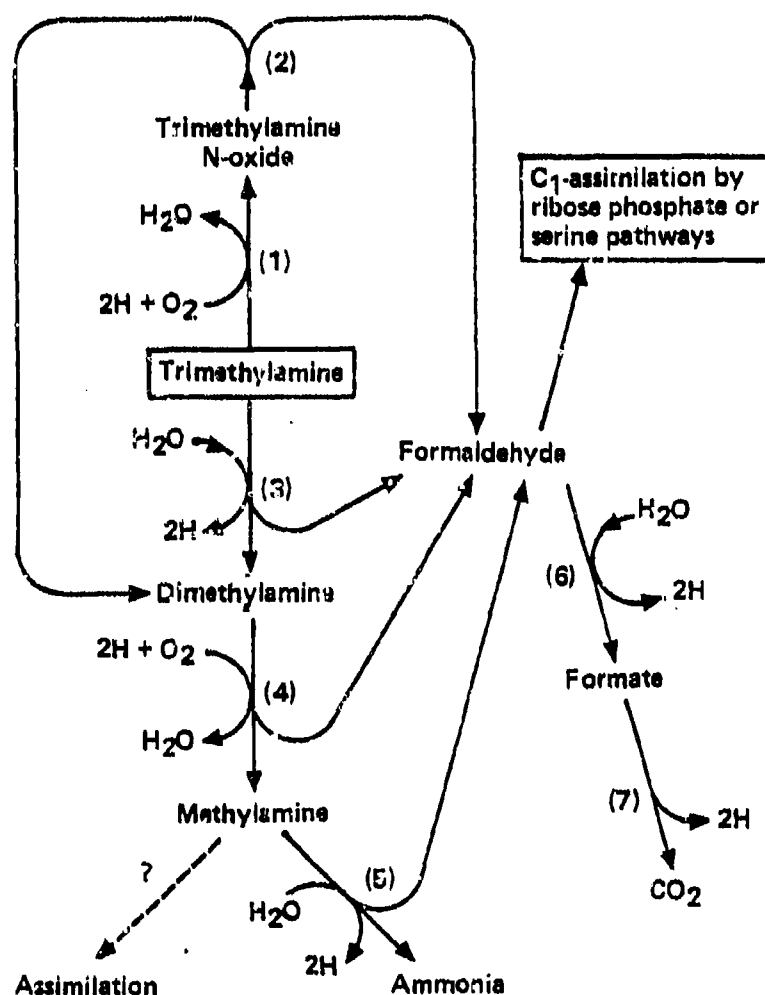
Trimethylamine-n-oxide demethylase catalyses the formation of formaldehyde and dimethylamine:



Dimethylamine is oxidized to methylamine and formaldehyde by an inducible secondary amine oxidase system:



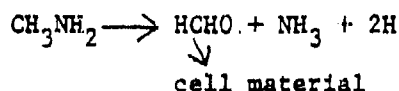
The further metabolism of methylamine involves oxidation to formaldehyde by one of two routes:



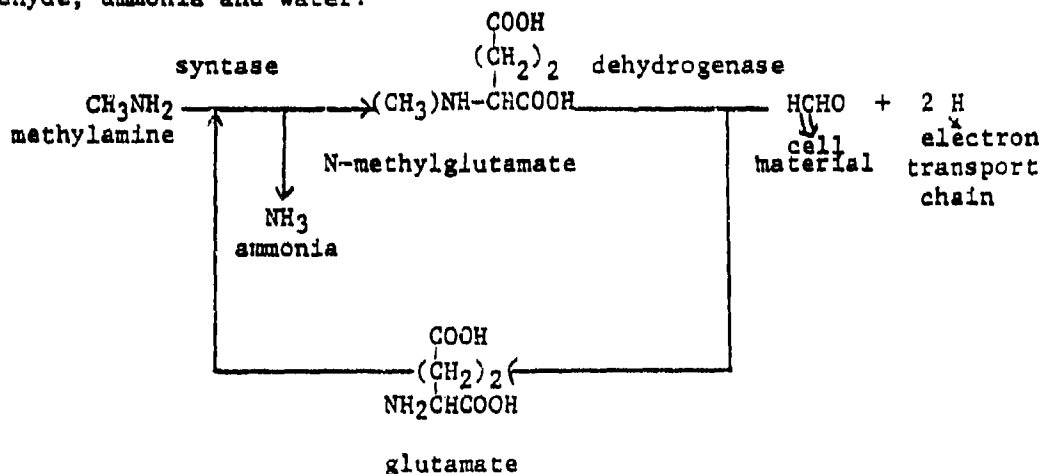
The enzymes of the pathways are: (1), trimethylamine mono-oxygenase; (2), trimethylamine N-oxide demethylase; (3), trimethylamine dehydrogenase; (4), dimethylamine mono-oxygenase; (5), primary amine dehydrogenase; (6), formaldehyde dehydrogenase; (7), formate dehydrogenase.

Figure IV-7. Oxidation of Trimethylamine by Obligate and Facultative Methylotrophs. (Colby and Zatman, 1973).

1) Primary amine dehydrogenase, a soluble enzyme, catalyses the oxidation of methylamine to formaldehyde and ammonia:



2) The N-methylglutamate system for methylamine oxidation consists of two inductible enzymes which affect the oxidation of methylamine to formaldehyde, ammonia and water:

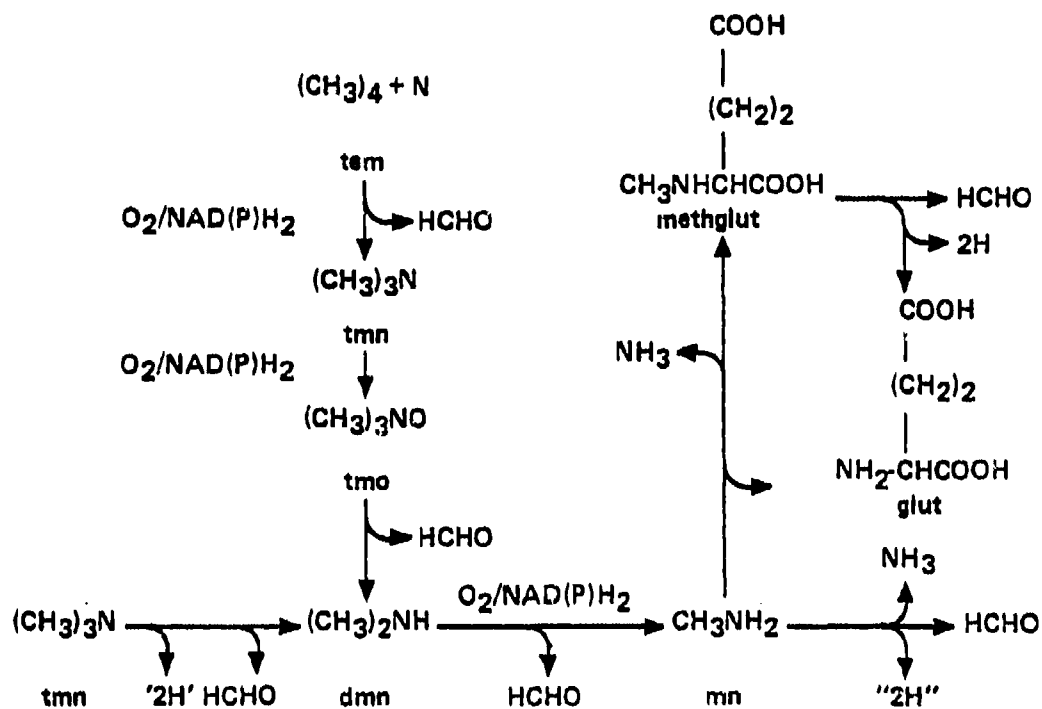


The oxidation of N-methyl compounds to formaldehyde, including alternate routes for methylamine oxidation, is illustrated in Figure IV-8 from Anthony (1975). The oxidation of one molecule of trimethylamine to dimethylamine and formaldehyde by obligate methylotrophs yields one molecule of reduced cofactor while the corresponding oxidation by facultative methylotrophs requires one molecule of reduced cofactor indicating that obligate methylotrophs use a more efficient pathway to harness metabolic energy (Colby and Zatman, 1973).

All of the microbial degradation pathways produce formaldehyde. The formaldehyde can then be oxidized to CO_2 or assimilated into cell material by means of the ribulose monophosphate cycle or the serine pathway. These pathways are described in Kitchens *et al.* (1976).

b. Formation of N-nitrosodimethylamine by Microorganisms

As discussed in Section D, nitrosation of dimethylamine can occur in acid solutions with a pH < 5. Under neutral conditions, N-nitrosodimethylamine formation in the environment is due to metabolism by microorganisms. Coloe and Hayward (1976) studied the formation of N-nitrosodimethylamine from dimethylamine and nitrite by various bacteria. The results of their study are presented in Table IV-12. The bacteria were incubated for 70 hours in a medium of 0.09 M dimethylamine and 0.1 M potassium nitrate. They found 81% of the strains were able to reduce nitrate and produce N-nitrosodimethylamine.



Abbreviations:

tem, tetramethyloxonium compounds
tmn, trimethylamine
tmo, trimethylamine N-oxide
dm, dimethylamine

mn, methylamine
glut, glutamate
methglut, N-methylglutamate

*Alternative routes for methylamine oxidation.

Figure IV-8. The Oxidation of N-methyl Compounds to Formaldehyde (Anthony, 1975).

Table IV-12. N-nitrosodimethylamine Production by Various Bacteria* (Coloe and Hayward, 1976).

Species	Number of Strains Tested	Number Producing NDMA			Average DMN Production (mM)	Range of NDMA Production (mM)		Number of nitratase-positive strains	Number of cultures viable at 70 h
		Any detectable amount	<0.22 mM	0.22-0.71 mM		Minimum	Maximum		
	42	42	0	7	35	0.54	6.08	42	5
	18	18	0	1	17	0.69	2.90	18	4
	2	2	0	2	0	0.60	0.62	2	0
	36	34	0	0	34	0.91	9.13	34	12
	22	20	0	3	17	0.55	2.95	20	7
	8	8	1	3	4	0.17	1.10	8	2
	12	12	1	3	8	0.216	1.57	12	4
	140	136	2	19	115	136	34

* 70-h cultures in defined medium supplemented with 0.09 M dimethylamine and 0.1 M potassium nitrate

Ayanaba *et al.* (1973) showed that N-nitrosodimethylamine was generated in samples of soil, lake water and sewage. In sewage, N-nitrosodimethylamine is produced when high dimethylamine and nitrite-N are present (Ayanaba and Alexander, 1974). The rates of N-nitrosodimethylamine formation as a function of dimethylamine and nitrite-N are shown in Figure IV-9. They also found N-nitrosodimethylamine formation in lake water as shown in Figure IV-10. The rate of formation increases as the pH decreases.

Mills and Alexander (1976) found N-nitrosodimethylamine present at levels greater than 1 ppm in 48 hours when sediment was initially exposed to levels of 250 ppm dimethylamine and 100 ppm nitrite. As shown in Figure IV-11, they observed similar levels of N-nitrosodimethylamine in sterile and non-sterile sediments. Therefore, bacteria were not necessary for the reaction to occur at a low pH. These studies indicate that the occurrence of nitrosamines is increased at a low pH in the presence of secondary amines and nitrate. High amounts of organic matter also seem to increase the levels of N-nitrosodimethylamine.

Data show that microorganisms in sewage or soil may contribute to the formation of a nitrosamine (*e.g.*, N-nitrosodimethylamine) in 1 of 3 ways:

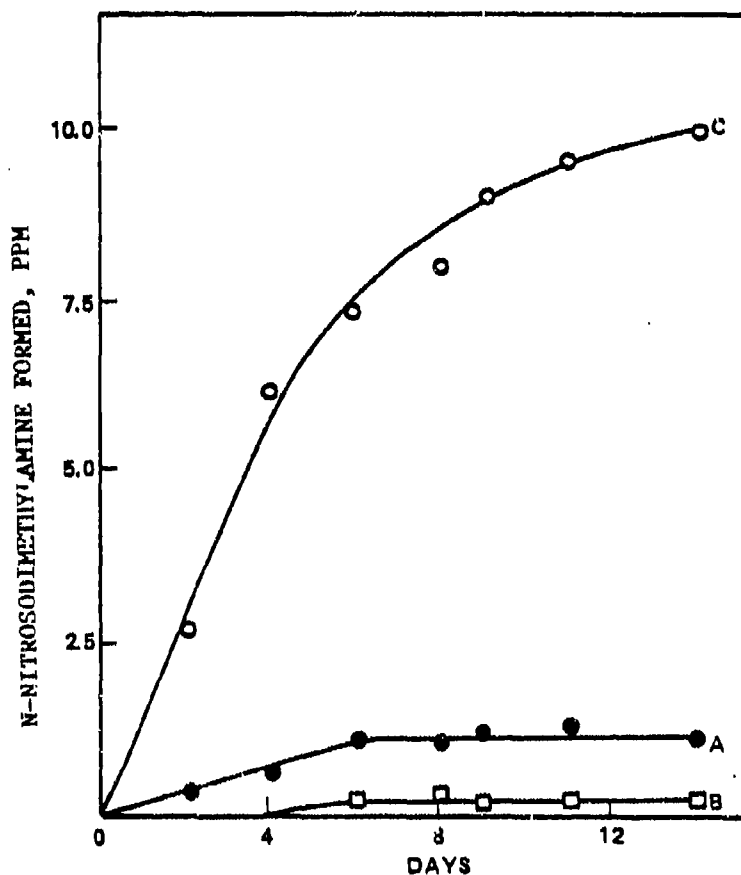
- 1) by converting 3° tertiary amines or other nitrogenous compounds to 2° secondary amines;
- 2) by forming nitrite through the reduction of nitrate or the oxidation of ammonium, the latter leading to appreciable nitrite accumulation in alkaline environments;
- 3) by causing an enzymatic reaction between nitrite and the 2° secondary amine.

Tate and Alexander (1976) reported that nitrosamines, once formed, are quite stable and may persist long enough to reach drinking or recreational waters. They can also be retained on the surfaces of root crops or be assimilated by higher plants.

4. Phototoxicity

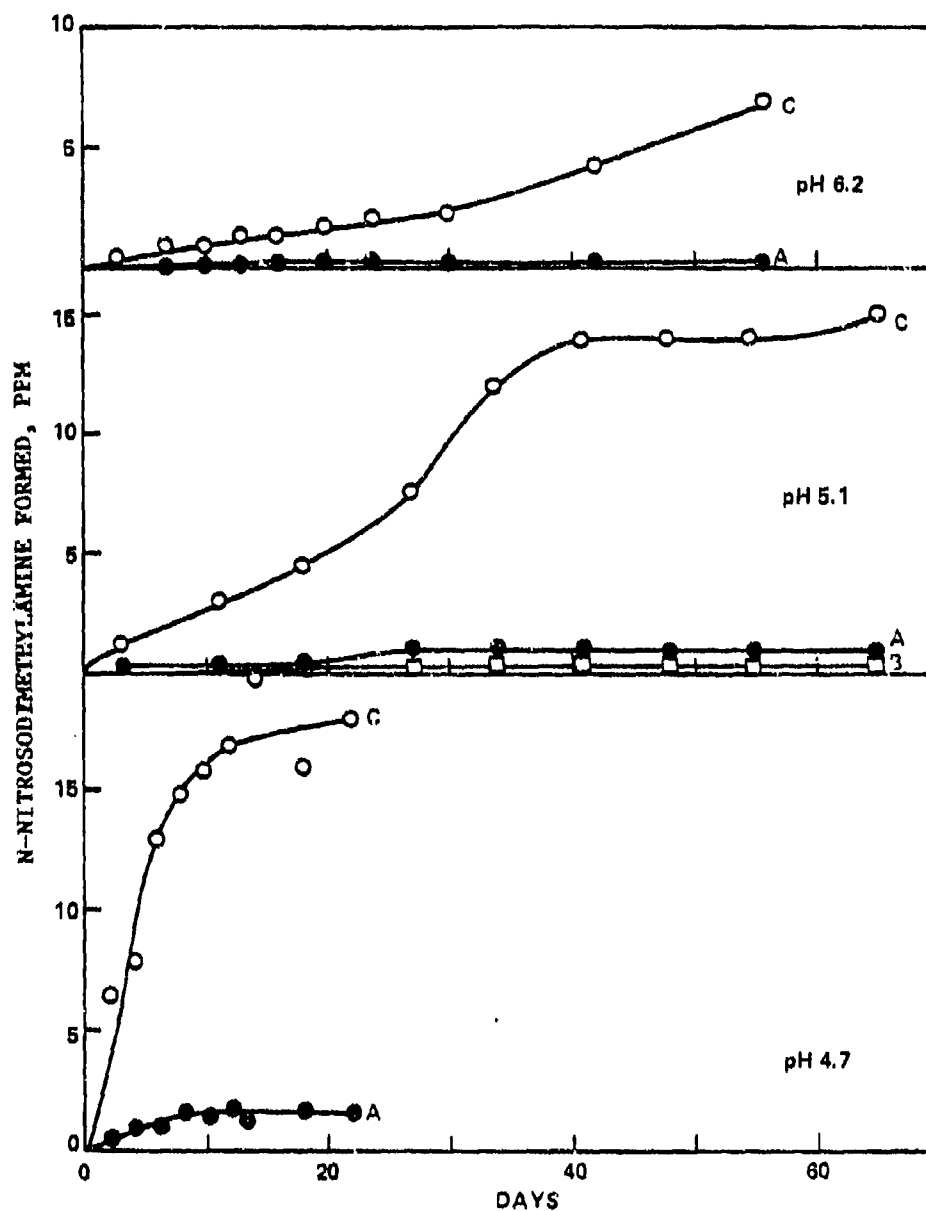
Only limited studies were uncovered on the toxicity of the methylamines to plants. Scheffer *et al.* (1968) demonstrated that methylamines can act as a C₁ precursor in sunflowers (*Helianthus annuus* L.). Tea plants (*Thea sinensis* L.) also possess the ability to metabolize micromolar amounts of methylamine. Formaldehyde can be produced from methylamine by the action of amine oxidase, which occurs widely in microorganisms, animals and higher plants (Hill and Mann, 1968; Kapeller-Adler, 1971). Abeliovich and Azor (1976) reported that methylamine uncoupled chloroplasts and reduced photosynthesis in algae. Significant penetration started at pH 8.0 and increased with elevation of the pH.

It is apparent from available literature that low concentrations of methylamine released to the environment would not be harmful to higher plants.



- A - 50 ppm dimethylamine-nitrogen and 100 ppm nitrite nitrogen
- B - 500 ppm dimethylamine-nitrogen and 10 ppm nitrite nitrogen
- C - 500 ppm dimethylamine-nitrogen and 100 ppm nitrite nitrogen

Figure IV-9. N-nitrosodimethylamine Formation in Sewage
(Ayanaba and Alexander, 1974).



A - 50 ppm dimethylamine-nitrogen and 100 ppm nitrite nitrogen
 B - 500 ppm dimethylamine-nitrogen and 10 ppm nitrite nitrogen
 C - 500 ppm diemthylamine-nitrogen and 100 ppm nitrite nitrogen

Figure IV-10. Formation of N-nitrosodimethylamine in Samples of Lake Water of Differing Acidities. (Ayanaba and Alexander, 1974)

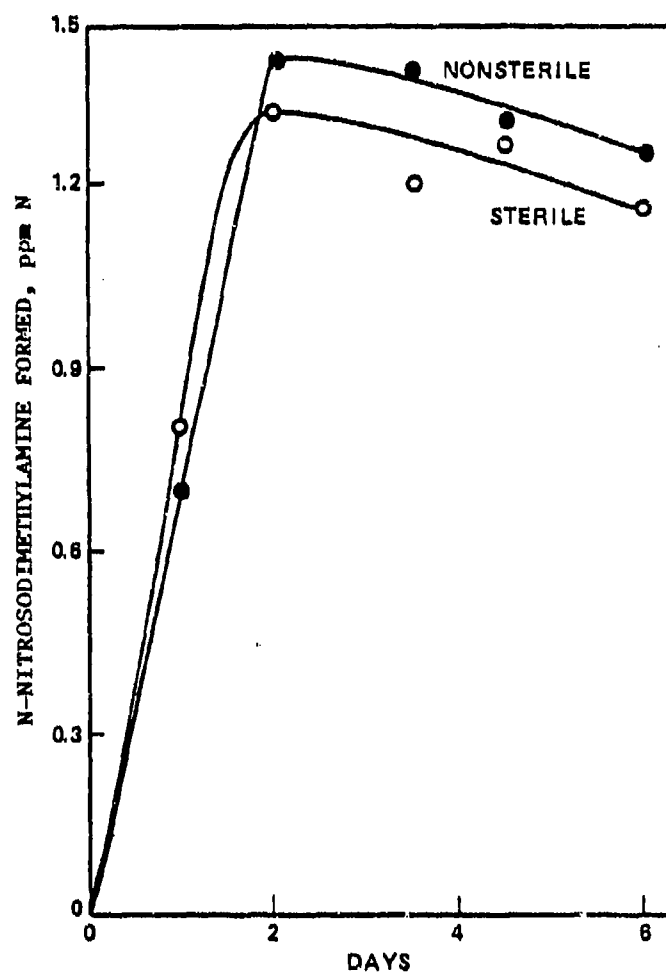


Figure IV-11. Formation of N-nitrosodimethylamine in Sterile and Nonsterile Langford Soil. (Mills and Alexander, 1976)

5. Availability of Literature for Phase II

The toxicological and environmental properties of the methylamines have been thoroughly investigated. Therefore, there is sufficient literature available for Phase II detailed toxicological and environmental study.

I. Regulations and Standards

1. Air and Water Standards

EPA has set effluent guidelines for the quantity and quality of pollutants which may be discharged from the manufacture of the methylamines. These effluent limitations are listed in Table IV-13.

Table IV-13. Quantity and Quality of Effluents Which May Be Discharged from the Manufacture of the Methylamines (Federal Register, 1974a).

Effluent Characteristic	Effluent Limitations	
	Maximum for Any One Day	Avg. of Daily Values for 30 Consecutive Days Shall Not Exceed -
	Pounds per 1000 lb of Product	
BOD ₅	0.13	0.058
TSS	0.20	0.088
pH	Within the range 6.0 to 9.0	

The methylamines are listed in EPA "Toxic Substances Control Act Candidate List of Chemical Substances" (1976). However, no new studies on these compounds are planned by EPA at this time.

2. Occupational Exposure Limits

The Occupational Safety and Health Administration has adopted the following threshold limits for exposure to the methylamines.

- methylamine - 10 ppm in air (Federal Register, 1974b)
- dimethylamine - 10 ppm in air (Federal Register, 1974b)
- trimethylamine - 25 ppm in air (American Conference of Governmental Industrial Hygienists, 1977)

The Soviet workplace limit for trimethylamine is 2.5 ppm (American Conference of Governmental Industrial Hygienists, 1977).

The methylamines are not listed in NIOSH "Suspected Carcinogens" subfile (1975).

3. Department of Transportation

The Department of Transportation requires the following labels for shipment of the methylamines (Federal Register, 1976).

- methylamine: flammable gas
- dimethylamine: flammable liquid
- trimethylamine: flammable gas

J. Conclusions and Recommendations

From the data gathered and evaluated in this preliminary problem definition study, several conclusions can be drawn.

1. The methylamines are not military unique chemicals.
2. These compounds are not highly toxic in acute doses to mammals and most aquatic organisms.
3. The methylamines are naturally occurring chemicals and are widely spread throughout the ecosystem.
4. Many organisms possess metabolic pathways for converting the methylamines into CO_2 and NH_3 or cellular material.
5. The highly potent carcinogen, N-nitrosodimethylamine, can be formed in the environment from trimethylamine or dimethylamine in the presence of nitrate or nitrite. These reactions require either a low pH or microbial activity.
6. The quantity of methylamines discharged at Holston is minor when compared to the overall Civilian and natural pollution from methylamines. However, when the A-1 still is operating, methylamine pollution in the local aquatic system is dangerously high.
7. Due to the high concurrent nitrate release at Holston AAP, N-nitrosodimethylamine could form in portions of the Arnett Branch and the Holston River. The extent of the nitrosamine formation in the Holston area ecosystem is unknown.

Although the quantity of methylamine discharged by Holston AAP is minor when compared to the overall Civilian pollution, the methylamines present a major problem to the local ecosystem. This problem is due to the highly concentrated sporadic discharge of these compounds and the potential for nitrosamine formation. Thus it is recommended that a detailed literature evaluation of the environmental fate of the methylamines be undertaken in Phase II. This literature evaluation should be supplemented with sampling and analysis data from Holston. Specific measurements of the methylamine, N-nitrosodimethylamine, nitrate and nitrite concentrations should be made at the outfall on Arnett Branch, at one point along the Branch and in the Holston River.

Measurements should also be made in order to determine if methylamine or methylamine derivatives are in the effluents from the E-Buildings.

From the data obtained in this study, Phase II detailed evaluation of the toxicological properties of the methylamines should be a low priority. The toxicity of these chemicals has been widely studied. Since the Army is not a user or intentional producer of these compounds, it is recommended that further toxicity studies on the methylamines should be carried out by the Civilian community.

K. References

- Abeliovich, A. and Azor, Y. (1976), "Toxicity of Ammonia to Algae in Sewage Oxidation Ponds," *Appl. Environ. Microbiol.*, 31(6), 801.
- Adams, A.P., and Whiting, J.H. (1976), "The Effect of Hexamethylenetetramine and Copper Ion on the Nitrification of Effluents from the Manufacture of RDX and HMX," U.S. Army Dugway Proving Ground, Dugway, Utah DPG-FR-X 911P.
- American Conference of Governmental Industrial Hygienists (1977), *Documentation of the Threshold Limit Values for Substances in Workroom Air*, 3rd ed.
- Anthony, C. (1975), "The Biochemistry of Methylophilic Micro-organisms," *Sci. Prog.*, Oxf, 62, 167.
- Avanaba, A. and Alexander, M. (1974), "Transformations of Methylamines and Formation of a Hazardous Product, Dimethylnitrosamine, in Samples of Treated Sewage and Lake Water," *J. Environ. Quality*, 3(1), 83.
- Ayanaba, A.; Verstraete, W. and Alexander, M. (1973), "Formation of Dimethylnitrosamine, a Carcinogen and Mutagen, in Soils Treated with Nitrogen Compounds," *Soil Sci. Soc. Amer. Proc.*, 37, 565.
- Ball, D.F. and Purnell, C.J. (1976), "The Use of Low Temperature Matrix Isolation Infrared Spectroscopy for the Identification and Measurement of Air-borne Amines," *Intern. J. Environ. Studies*, 9, 131.
- Bouyoucos, S.A. (1977), "Determination of Ammonia and Methylamines in Aqueous Solutions by Ion Chromatography," *Anal. Chem.*, 49(3), 401.
- Bovet, D. and Bovet-Nitti, F. (1948), *Medicaments du Systeme Nerveux Vegetatif*, S. Karger Pub. Co., New York, in NIOSH (1976) "Registry of Toxic Effects of Chemical Substances", Office of Research and Standards Development.
- Burg, A. B. (1943), "The Behavior of Trimethylamine, Trimethylammonio-sulfur Trioxide and Trimethylamine Oxide toward Sulfur Dioxide," Department of Chemistry at the University of Southern California.
- Calvert, J. and Pitts, J. (1967), *Photochemistry*, John Wiley and Sons, New York.
- Chemical Week (1977), "Alkylamines Ride on Ag Chemical Growth," *Chem. Week*, March 16.
- Colby, J. and Zatman, L.J. (1973), "Trimethylamine Metabolism in Obligate and Facultative Methylophilic," *Biochem. J.*, 132, 101.
- Coloe, P.J. and Hayward, N.J. (1976), "The Importance of Prolonged Incubation for the Synthesis of Dimethylnitrosamine by Enterobacteria," *J. Med. Microbiol.*, 9(2), 211.

Commercial Solvents Corporation (1965), *Methylamines*.

Department of Transportation (1974), CHRIS List.

Dunn, S.R.; Simenhoff, M.L. and Wesson Jr., L.G. (1976), "Gas Chromatographic Determination of Free Mono-, Di- and Trimethylamines in Biological Fluids," *Anal. Chem.*, 48(1), 41.

Dzanashvili, G. (1967), "Maximum Permissible Concentration of Dimethylamine in Water Bodies," *Hyg. Sanit.*, 32(6), 329.

EPA (1976), "Toxic Substances Control Act PL94-469, Candidate List of Chemical Substances."

Evans III, F.L., ed. (1975), *Ozone in Water and Wastewater Treatment*, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 44.

Federal Register (1974a), 39, 14685.

Federal Register (1974a), 39, 23540.

Federal Register (1976), 41, 57018.

Gillette, L.A.; Miller, D.L. and Redman, H.E. (1952), "Appraisal of a Chemical Waste Problem by Fish Toxicity Tests," *Sew. Ind. Wastes*, 24(11), 1397.

Grabinska-Loniewska, A. (1974), "Studies on the Activated Sludge Bacteria Participating in the Biodegradation of Methanol, Formaldehyde and Ethylene Glycol, II. Utilization of Various Carbon and Nitrogen Compounds," *ACTA Microbiologica. Pol.*, Ser. B, 6(23), 83.

Gruger Jr., E.H. (1972), "Chromatographic Analyses of Volatile Amines in Marine Fish," *J. Agr. Food Chem.*, 20(4), 781.

Hanst, P.L.; Spence, J.W. and Miller, M. (1977), "Atmospheric Chemistry of N-nitroso Dimethylamine," *Environ. Sci. Technol.*, 11(4), 403.

Hawley, G.C. (1977), *The Condensed Chemical Dictionary*, 9th edition, Van Nostrand Reinhold, Co., New York.

Hill, J.M. and Mann, P.J. (1968), *Recent Aspects of Nitrogen Metabolism in Plants*, Academic Press, New York. in Suzuki, T. (1973), "Metabolism of Methylamine in the Tea Plant (*Thea sinensis* L.)," *Biochem. J.*, 132, 753.

Ishiwata, H.; Tanimura, A. and Ishidate, M. (1975), "Studies on *In Vivo* Formation of Nitroso Compounds (V). Formation of Dimethylnitrosamine from Nitrate and Dimethylamine by Bacteria in Human Saliva," *J. Food Hyg. Soc.*, 16(4), 234.

- Kapeller-Adler, R. (1971), *Analysis of Biogenic Amines and Their Related Enzymes*, John Wiley and Sons, New York, in Suzuki, T. (1973), "Metabolism of Methylamine in the Tea Plant (*Thea sinensis* L.)," *Biochem. J.*, 132, 753.
- Khramova, S.I. and Bokarev, K.S. (1976), "Gas Chromatographic Determination of Residual Amounts of Amines in Plants," *Fizol. Rast. (Mosc.)*, 23(3), 625.
- Kitchens, J.F.; Casner, R.E.; Edwards, G.S.; Harward III, W. and Macri, B.S. (1976), "Investigation of Selected Potential Environmental Contaminants: Formaldehyde," Final Report, U.S. EPA, Washington, DC 20460, EPA-560/2-76-00g, ARC 49-5681.
- Kitchens, J.F. and Valentine, R.S. (1974), "Methyl Nitrate Removal Study," Final Report to Holston Defense Corporation, Atlantic Research Corporation, P.O. 103-0121.
- Klubes, P. and Jondorf, W.R. (1971), "Dimethylnitrosamine Formation from Sodium Nitrite and Dimethylamine by Bacterial Flora of Rat Intestine," *Research Communications in Chemical Pathology and Pharmacology*, 2(1), 24.
- Lane, R.P. and Bailey, M.E. (1973), "The Effect of pH on Dimethylnitrosamine Formation in Human Gastric Juice," *Jd Cosmet. Toxicol.*, 11, 851.
- Leonard Process Co., Inc., (1978) letter from Ian Williams.
- Lijinsky, W. and Singer, G.M. (1974), *Formation of nitrosamines from tertiary amines and nitrous acid*. In: Bogovski, P and Walker, E.A., eds, *N-Nitroso Compounds in the Environment*, Lyon, International Agency for Research on Cancer (IARC Scientific Publications No. 9), pp. 111-114.
- Lowenheim, F.A. and Moran, M.K. (1975), *Frith, Keyes and Clark's Industrial Chemicals*, 4th edition, John Wiley and Sons, New York, 55.
- March, J. (1968), *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, McGraw-Hill, New York.
- Miller III, A.; Scanlan, R.A.; Lee, J.S. and Libbey, L.M. (1972), "Quantitative and Selective Gas Chromatographic Analysis of Dimethyl- and Trimethylamine in Fish," *J. Agr. Food Chem.*, 20(3), 709.
- Mills, A.L. and Alexander, M. (1976), "Factors Affecting Dimethylnitrosamine Formation in Samples of Soil and Water," *J. Environ. Qual.*, 5(4), 437.
- Mirvish, S.S. (1970), "Kinetics of Dimethylamine Nitrosation in Relation to Nitrosamine Carcinogenesis," *J. Nat. Cancer Inst.*, 44, 633.
- Morrison, R. and Boyd, R. (1973), *Organic Chemistry*, 2nd ed., Allyn and Bacon, Inc., Boston.
- Mosier, A.R.; Andre, C.E. and Viets Jr., F.G. (1973), "Identification of Aliphatic Amines Volatilized from Cattle Feedyard," *Environ. Sci. Technol.*, 7, 642.

- NIOSH (1975), "Suspected Carcinogens, A Subfile of the NIOSH Toxic Substances List," U.S. Department of Health, Education and Welfare.
- NIOSH (1977), "Registry of Toxic Effects of Chemical Substances," U.S. Department of Health, Education and Welfare.
- Okita, T. (1970), "Filter Method for the Determination of Trace Quantities of Amines, Mercaptans and Organic Sulphides in the Atmosphere," *Atmospheric Environ.*, 4, 93.
- Onuska, I.I. (1973), "Gas Chromatographic Determination of Aliphatic Amines and Quantitative Analysis of Small Amounts of Dimethylamine in Wastewater," *Water Research*, 7, 835.
- Pouchert, C.J. (1975), *The Aldrich Library of Infrared Spectra*, Aldrich Chemical Co., Inc.
- Roller, P.P. and Keefer, L.K. (1973), "Catalysis of Nitrosation Reactions by Electrophilic Species," *Int. Agency for Research in Cancer Science*, Publication No. 9, 86.
- Ruiter, A. and Weseman, J.M. (1976), "The Automated Determination of Volatile Bases (Trimethylamine, Dimethylamine and Ammonia) in Fish and Shrimp," *J. Ed. Technol.*, 11, 59.
- Sakevich, A.F. (1970), "Detection of Methyl Amines in the Culture of *Stephanodiscus hantzschii*," *Gidrobiol. Zh.*, 6(3), 98, from Chem. Abstr. 73-117155C.
- Sasajima, M. (1968), "Studies on Psychrotolerant Bacteria in Fish and Shellfish III. Reduction and Decomposition of Trimethylamine oxide by Psychrotolerant Bacteria," *Tok. Suisan Kenk. Ken. Hok.*, 55, 205, from Chem. Abstr. 73:32608 (1970).
- Sax, N.I., ed. (1976), *Dangerous Properties of Industrial Materials*, 4th ed., Van Nostrand Reinhold Publ. Corp., New York.
- Scanlan, R.A.; Lohsen, S.M.; Bills, D.D. and Libbey, L.M. (1974), "Formation of Dimethylnitrosamine from Dimethylamine and Trimethylamine at Elevated Temperatures," *J. Agr. Food Chem.*, 22(1), 148.
- Scheffer, F.; Kickuth, R. and Aldag, R. (1968), "Aufnahme und Metabolisierung von C^{14} -Methylamin und DL-N- C^{14} -Methyl-Valin Durch *Helianthus Annuus* L.," *Plant Soil*, 28(3), 442.
- Simenhoff, M.L. (1975), "Metabolism and Toxicity of Aliphatic Amines," *Kidney Intl.*, 7, S-314.

- Singer, G.M. and Lijinsky, W. (1976), "Naturally Occurring Nitrosable Amines, II. Secondary Amines in Tobacco and Cigar Smoke Condensate," *J. Agr. Food Chem.*, 24(3), 550, 553.
- Smith, T.A. (1971), "The Occurrence, Metabolism and Functions of Amines in Plants," *Biol. Rev.*, 46, 201.
- S.R.I. (1977a), *Dictionary of Chemical Producers*, Stanford Research Institute, Menlo Park, CA.
- S.R.I. (1977b), *Chemical Origins and Markets*, 5th ed., Stanford Research Institute, Menlo Park, CA.
- Stecker, P. (1968), *The Merck Index, An Encyclopedia of Chemicals and Drugs*, 8th ed., Merck & Co., Rahway, New Jersey.
- Tate III, R.L. and Alexander, M. (1976), "Microbial Formation and Degradation of Dimethylamine," *Appl. Environ. Microbiol.*, 31(3), 399.
- Terenin, A. and Villesov, F. (1963), "Photoionization and Photodissociation of Aromatic Molecules by Vacuum Ultraviolet Radiation," from W.A. Noyes, ed., *Advances in Photochemistry*, Vol. 2, 285.
- USAEHA (1971), "Waste Flow Characterization, Area B, Holston Army Ammunition Plant, Kingsport, Tennessee," Letter Report and Attachments.
- Warner, M.; Randall, W.F.; Diehl, S.A.; Pearson, J.G. and Meier, E.P. (1978), "Acute Toxicity of Several Munitions Related Compounds to *Daphnia Magna*, Fathead Minnows and Green Sunfish," Draft, U.S. Army Research and Development Laboratory, Technical Report.
- Windholz, M. (1976), *The Merck Index*, 9th ed., Merck & Co., Inc., Rahway, New Jersey.

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

HEXAHYDRO-1,3-DINITRO-5-ACETYL-S-TRIAZINE (TAX)

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

HEXAHYDRO-1,3-DINITRO-5-ACETYL-S-TRIAZINE (TAX)

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Best Available Copy

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

SUMMARY

TAX (hexahydro-1,3-dinitro-5-acetyl-s-triazine) is a by-product of the RDX manufacture at Holston Army Ammunition Plant. It is formed during the nitrolysis of hexamine. During this process, a portion of the hexamine is also acetylated by the acetic acid/acetic anhydride solvent. TAX is present in the effluent stream from the RDX dewatering and incorporation process. The concentration of TAX in these effluents is 60 to 90% of the RDX concentration and 1.6 to 1.8 times the HMX concentration. Thus, at full mobilization, the quantity of TAX in Holston's effluent would be significant. Since TAX is not produced or used by the civilian community, it is a military unique compound.

The information on the physical, chemical and toxicological properties of TAX is very limited. Many of its properties can only be inferred by comparison to those of RDX and HMX. TAX appears to be more water soluble than RDX or HMX although no specific numbers are available. Thus, TAX would be more available to aquatic life than RDX or HMX and may exhibit a highly toxic effect on the organisms in the Holston River.

Due to the military uniqueness of this compound, it is recommended that the following studies be initiated by the Army.

- Phase II detailed evaluation of the toxicological and environmental hazards of TAX
- solubility studies in water
- further sampling and analysis of TAX at Holston AAP
- the effect on the proposed biotreatment facility be evaluated
- the biotransformation products of TAX in this facility be determined
- *in vitro* mutagenic studies
- acute aquatic toxicity studies
- acute and chronic mammalian toxicity studies

FOREWORD

This report details the results of a preliminary problem definition study on TAX. The purpose of this study was to determine the Army's responsibility for conducting further research on TAX in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on TAX, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

TAX was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

TABLE OF CONTENTS

	<u>Page</u>
Summary	V-3
Foreword	V-5
A. Alternate Names	V-9
B. Physical Properties	V-9
C. Chemical Properties	V-10
1. Synthesis	V-10
2. General Reactions	V-11
3. Environmental Reactions	V-12
4. Sampling and Analysis	V-12
D. Uses of TAX in Munitions Production	V-12
1. Uses	V-12
2. Occurrences of TAX in the Aqueous Effluents from HAAP	V-13
E. Uses in the Civilian Community	V-13
F. Comparison of Civilian and Military Uses and Pollution of TAX	V-13
G. Toxicological and Environmental Hazards	V-15
1. Mammalian Toxicity	V-15
2. Aquatic Toxicity	V-15
3. Availability of Literature for Phase II	V-15
H. Regulations and Standards	V-15
I. Conclusions and Recommendations	V-15
J. References	V-17

LIST OF TABLES

<u>Number</u>		<u>Page</u>
1	Physical Properties of TAX	V-9
2	Analysis of Waste Streams for RDX, HMX and TAX	V-14

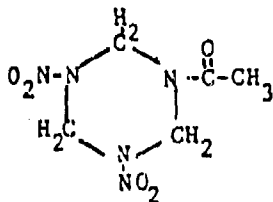
LIST OF FIGURES

<u>Number</u>		<u>Page</u>
1	Ultraviolet Spectrum of TAX	V-10

V. TAX - HEXAHYDRO-1,3-DINITRO-5-ACETYL-s-TRIAZINE

A. Alternate Names

TAX is a by-product in the manufacture of RDX. This compound is a substituted symmetrical triazine having a molecular formula of $C_5H_9N_5O_5$ and the following structural formula:



The molecular weight of TAX is 219.15 g/mole. Pertinent alternate names for TAX are listed below:

CAS Registry No.: 14168-42-4

CA Name (9CI): 1,3,5-triazine,1-acetylhexahydro-3-5-dinitro

Wiswesser Line Notation:

Synonyms: TAX

B. Physical Properties

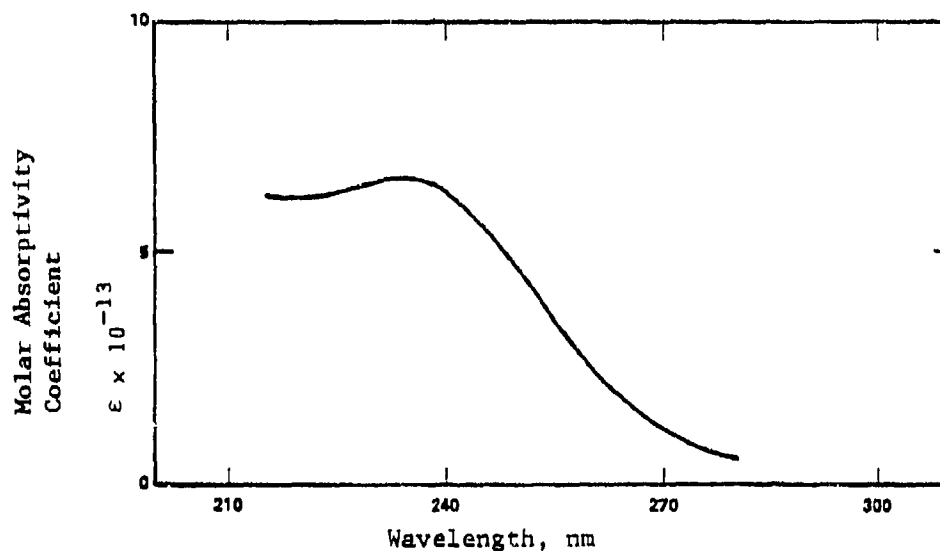
Available physical properties of TAX are listed in Table V-1. The ultraviolet absorption spectrum of TAX is shown in Figure V-1.

Table V-1. Physical Properties of TAX. *

Physical form @ 20°C:	solid, prismatic plates
Color:	colorless
M.P.:	156 - 158°C
IR (KBr):	3060, 1660, 1580, 1420, 1370, 1280, 1240, 1180, 11030, 990, 920, 880, 850, 810, 750, 630, 585, 490 cm ⁻¹
NMR:	δ 6.25 (singlet, 2H, (O ₂ NN) ₂ -CH ₂) δ 5.80 (singlet, 4H, (O ₂ NN)-CH ₂ -NCO-) δ 2.27 (singlet, 3H, -CH ₃)

* References: Dunning and Dunning, 1950; Chapman *et al.*, 1949; Aristoff *et al.*, 1949.

Figure V-1. Ultraviolet Spectrum of TAX (Schroeder *et al.*, 1951)

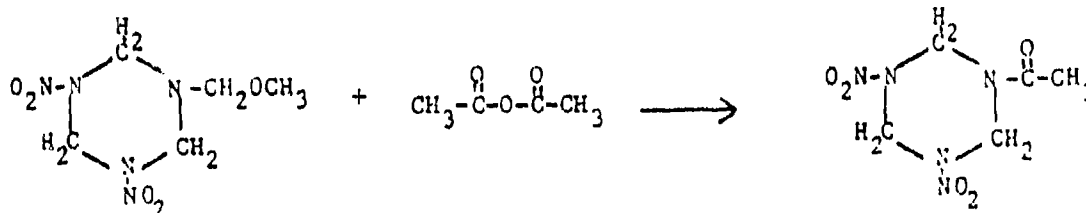


C. Chemical Properties

1. Synthesis

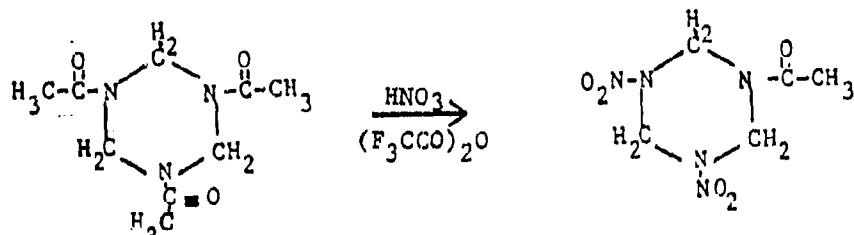
TAX has been synthesized by a number of investigators. Chapman *et al.* (1949) used methylene dinitroamine as their starting material. Following treatment with dry formaldehyde at 0°C, an ether solution of anhydrous ammonia was added to the methylene dinitroamine. The solid product was refluxed for 30 minutes with acetylchloride. The resulting material was filtered, dried, and recrystallized from methanol to yield pure TAX.

Dunning and Dunning (1950) treated 1-methoxymethyl-3,5-dinitro-hexahydro-1,3,5-triazine with acetic anhydride to form TAX.



The crude product was washed with ether, dried *in vacuo* and recrystallized from ethyl acetate.

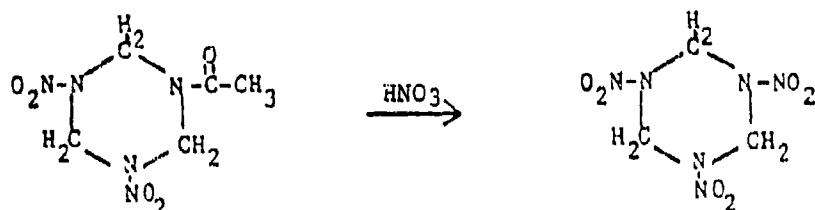
Gilbert *et al*, (1975) prepared TAX in 93% yield from 1,3,5-triacylhexahydro-1,3,5-triazine.



Nitric acid was added dropwise to a mixture of 1,3,5-triacetylhexahydro-1,3,5-triazine and trifluoroacetic anhydride. The temperature was maintained below 40°C with a cooling bath. The reaction was allowed to run one hour. TAX was filtered, dried, and recrystallized from isopropanol.

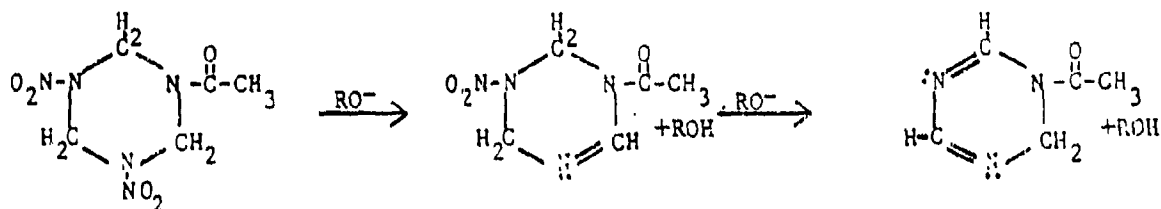
2. General Reactions

Treatment of TAX with nitric acid yields RDX (Aristoff *et al*, 1949).



The reaction of secondary nitramines with alkoxide anion has been investigated (Stals, 1969). The base abstracts a methylene proton to form the carbanion which undergoes intramolecular displacement of NO_2^- .

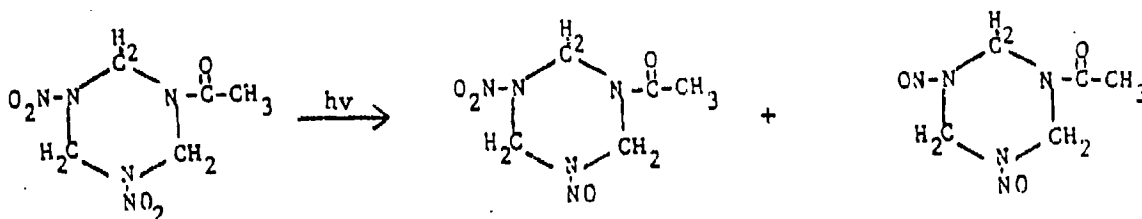
Analogous reaction of TAX with base would give the following products.



TAX is decomposed by boiling in concentrated sulfuric acid (Aristoff *et al*, 1949).

3. Environmental Reactions

The photolysis of dimethylnitramine has been reported (Suryanarayanan and Bulusu, 1970). Irradiation in either ethanol, n-hexane, or acetonitrile yields dimethylnitrosamine. An analogous photodecomposition of TAX would lead to two products.



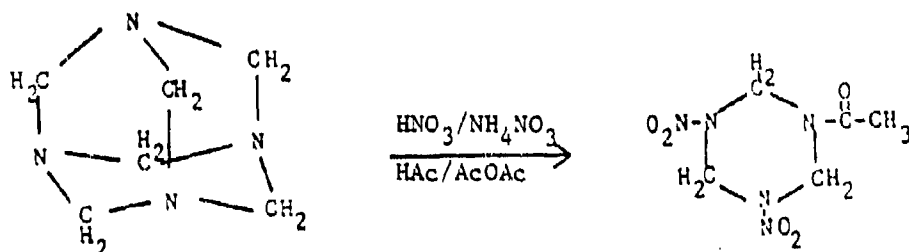
4. Sampling and Analysis

Quantitative analysis of TAX is best performed by instrumental methods. Monitoring for TAX in the wastewater at Holston AAP is accomplished using high pressure liquid chromatography (Holston Defense Corporation, 1978). Samples are obtained by extraction with a methylene chloride: acetonitrile (88:12) mixture. Detection of μg per liter amounts is possible.

D. Uses of TAX in Munitions Production

1. Uses

TAX is not used or purposely produced by the military. It is an unwanted by-product in the manufacture of RDX at Holston Army Ammunition Plant (HAAP). TAX is formed during the nitration of hexamine in the presence of nitric acid/ammonium nitrate and acetic acid/acetic anhydride to produce RDX. During this process, some of the hexamine is acetylated by the acetic acid/acetic anhydride solvent.



Some TAX probably ends up in the final RDX product. This TAX could also be a pollutant at RDX loading (LAP) plants. However, the amount of TAX in the product is unknown.

2. Occurrences of TAX in the Aqueous Effluents from HAAP

In 1977, Holston Defense Corporation began sampling several effluent streams for TAX. The data they obtained depended to a large extent on the manner in which the samples were stored. For comparison purposes, only the analytical results from the samples stored in acetonitrile are presented in Table V-2. Samples were obtained from four locations:

- N-3 - manhole below Building N-3 which carries effluents from the G, H, I, J, K, M and N Buildings on lines 1 through 5.
- N-6 - manhole below Building N-6 which carries process effluents from Buildings D6, E6, and G6.
- T-2 - manhole below T-2 (acid area) which carries process effluents from buildings C3, C5, B9, B11, D3, D5, E3 and E4.
- Holston River at the area B Boundary.

From the data in the table, it appears that TAX is entering the environment from the nitration buildings (D-Buildings), the Acids Removal and Explosives Wash (E-Buildings), Recrystallization (G-Buildings), Dewatering (H-Buildings) and the Incorporation Buildings (I, J, K, L, M). However, the major amount of TAX entering the environment is from the dewatering and incorporation steps.

Average concentrations of RDX, TAX and HMX at the four sample points are given below.

<u>Sample Point</u>	<u>RDX(mg/l)</u>	<u>TAX(mg/l)</u>	<u>HMX(mg/l)</u>
N-3	5.5	4.8	2.6
N-6	4.5	2.6	1.6
T-2	0.3	0.02	0.12
River	0.01	0.004	0.01

In the effluent from the dewatering and incorporation steps, TAX is present at levels of between 60 and 90% of the RDX content. At full mobilization ~ 208 million pounds of RDX would be produced each year. If 1% of this amount is lost in the effluents, then HAAP could discharge as much as 2.1 million pounds of RDX per year. Discharges of TAX could be 1.3 to 1.9 million pounds per year if the 60 - 90% ratio of TAX/RDX is valid.

E. Uses in the Civilian Community

There are no uses or production of TAX in the civilian community.

F. Comparison of Civilian and Military Uses and Pollution of TAX

TAX is a by-product of RDX production at HAAP. There are no civilian uses or production of this chemical. Thus, TAX is a unique military by-product which enters the environment in the effluents from HAAP.

Table V-2. Analysis of Waste Streams for RDX, HMX, and TAX
(Holston Defense Corporation, 1978).

Date	Sample Point	RDX	TAX	HMX
5/17-18/77	N-3	10.0	8.7	2.2
	N-6	6.3	6.3	1.3
	T-2	0.2	-	0.04
	River	0.01	0.003	-
5/24-25/77	N-3	7.2	16.9	2.4
	N-6	2.2	2.2	1.3
	T-2	0.4	-	2.6
	River	0.007	0.003	0.03
5/31/77-6/1/77	N-3	2.4	-	4.5
	N-6	7.0	3.1	2.1
	T-2	0.4	-	0.07
	River	0.006	-	0.006
6/6-7/77	N-3	4.3	-	1.5
	N-6	5.6	5.6	1.7
	T-2	0.4	0.007	0.1
	River	0.009	0.003	0.006
6/8-9/77	N-3	2.1	2.2	0.3
	N-6	1.0	1.0	0.4
	T-2	0.1	0.005	0.03
	River	0.0005	0.01	0.0009
6/13-14/77	N-3	10.4	5.8	2.9
	N-6	3.9	0.007	2.4
	T-2	0.2	0.04	-
	River	0.02	0.001	0.01
6/17-19/77	N-3	1.8	0.007	4.7
	N-6	5.3	3.4	2.3
	T-2	0.3	0.1	-
	River	0.02	0.005	0.03

G. Toxicological and Environmental Hazards

1. Mammalian Toxicity

No mammalian toxicity studies on TAX are reported in the literature. However, studies on RDX have been reported (Von Oettingen *et al*, 1949). These studies show a low acute toxicity of RDX. Chronic exposure by respiratory, gastrointestinal, or skin absorption results in nausea, vomiting, convulsions and unconsciousness in human workers. A 1.5 mg/m³ TLV has been recommended for RDX (American Conference of Governmental Industrial Hygienists, 1977). A similar TLV for TAX would probably provide adequate worker protection.

2. Aquatic Toxicity

While no acute toxicity data exists for TAX, Liu and Bailey (1977) studied the toxicity of RDX. They found a 96 hour LC50 to minnows of 5.3 ppm and a 48 hour EC50 to *Daphnia* >41 ppm. It is likely that the acute toxicity of TAX to aquatic organisms is in a similar range. Liu and Bailey also found that RDX is not bioconcentrated to any great extent (2-3 times) by aquatic organisms. So it is probable that TAX also has a low bioconcentration factor. However, at full mobilization production the RDX/TAX concentrations in the Holston River are expected to be high enough to cause stress to the aquatic organisms.

Green and Eiklor (1977) found that 59% of the RDX added to a trickling filter is degraded. However, the products of the degradation were not identified. It is possible that highly toxic N-nitroso compounds are formed in this degradation. It is probable that TAX can be degraded by microorganisms and thus not accumulate in the aquatic system.

3. Availability of Literature for Phase II

There appears to be relatively little readily available literature on toxicity and environmental fate of TAX. However, contacts with foreign RDX manufacturers, evaluation of foreign literature and comparison with other nitramines might prove useful.

H. Regulations and Standards

There are no existing United States regulations or standards on TAX.

I. Conclusions and Recommendations

An evaluation of the readily available literature on TAX has shown it to be a military unique compound. Because of its presence in large quantities in the HAAP effluents, further study of this compound by the Army should be undertaken. The following studies are recommended.

1. Phase II detailed evaluation of the toxicological and environmental hazards of this compound should be undertaken. This study

should evaluate the older and the foreign literature on TAX and similar nitramines. Contacts with foreign manufacturers and researchers should also be made.

2. Solubility studies in aqueous media should be conducted if these values are not found in the older literature.

3. Further sampling and analysis of Holston effluents should be undertaken to verify existing data.

4. The effect of TAX on the proposed biotreatment facility as well as its biotransformation products should be determined.

5. Acute aquatic toxicity studies with this compound should be initiated on at least two species present in the Holston River.

6. *In vitro* mutagenic tests should be conducted on TAX.

7. Acute and chronic mammalian toxicity studies should also be conducted by both skin and oral routes of administration.

J. References

- American Conference of Governmental Industrial Hygienists (1977), "Documentation of the Threshold Limit Values for Substances in Workroom Air," 3rd Ed.
- Aristoff, E.; Graham J.A.; Meen, R.H.; Myers, G.S. and Wright, G.F. (1949), "Nitrolysis of Hexamethylenetetramine VI. Recombination of Fragments during Hexamethylenetetramine Nitrolysis in Acetic Anhydride," *Can. J. Res.*, 27B, 520.
- Chapman, F.; Owston, P.G. and Woodcock, D. (1949), "Studies on Nitroamines Part IV. The Reaction of Nitroamines with Formaldehyde and Primary or Secondary Amines," *J. Chem. Soc.*, 1638.
- Dunning, K.W. and Dunning, W.J. (1950), "Methylene-Nitramines. Part I. The Reaction of Hexamine Dinitrate with Nitric Acid at Low Temperatures," *J. Chem Soc.*, 2925.
- Gilbert, E.E.; Leccacorvi, J.R. and Warman, M. (1976), "The Preparation of RDX from 1,3,5-triacylhexahydro-s-triazines" in *Industrial and Laboratory Nitrations*, American Chemical Society Systems, series 22, 327.
- Green, J.M. and Eiklor, J.W. (1977), "Waste Management, Explosives Manufacturing and Finishing, Phase I.," Contract DAAA 09-73-C-0079.
- Holston Defense Corporate (1978), personal communication with R. Jackson and R. Hash.
- Liu, H.W. and Bailey, H.C. (1977), "Toxicity of TNT Wastewater to Aquatic Organisms," Monthly Progress Report No. 27, S.R.I. Project LSU-4262, Contract No. DAMD-17-75-C-5056.
- Schroeder, W.A.; Wilcox, P.E.; Trueblood, K.N. and Dekker, A.O. (1951), "Ultraviolet and Visible Absorption Spectra in Ethyl Alcohol," *Anal. Chem.*, 23(12), 1740.
- Stals, J. (1969), The Chemistry of Aliphatic Unconjugated Nitramines III. Thermal, Electrophilic, and Nucleophilic Reactions, *Australian J. Chem.*, 22, 2515.
- Suryanarayanan, K. and Bulusu, S. (1970), "Photochemical Studies of Secondary Nitramines I. Absorption Spectra of Nitramines and Photolysis of Dimethylnitramine in Solution", AD-712 992.
- Von Oettingen, W.F.; Donahue, D.D.; Yagoda, H.; Monaco, A.R. and Harris, M.R. (1949), "Toxicity and Potential Dangers of Cyclotrimethylene-trinitramine, *J. Ind. Hyg. and Tox.*, 31-21-31, in "Documentation of the Threshold Limit Values for Substances in Workroom Air, 1971, American Conference of Governmental Industrial Hygienists," 3rd Ed.

AD

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

OCTAHYDRO-1-ACETYL-3,5,7-TRINITRO-S-TRIAZINE (SEX)

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

AD

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

OCTAHYDRO-1-ACETYL-3,5,7-TRINITRO-S-TETRAZINE (SEX)

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1973

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7 57

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

SUMMARY

SEX (octahydro-1-acetyl-3,5,7-trinitro-s-tetrazine) is a by-product of the RDX/HMX manufacture at Holston Army Ammunition Plant. It is formed during the nitrolysis of hexamine. During this process, a portion of the hexamine is also acetylated by the acetic acid/acetic anhydride solvent.

In the effluent streams from the RDX/HMX dewatering and incorporation steps, SEX is present in approximately the same concentrations as HMX. Thus at full mobilization the quantity of SEX in Holston's effluent would be significant. Since SEX is not manufactured or used by the civilian community, it is a military unique compound.

The information on the physical, chemical and toxicological properties of SEX is very limited. Many of its properties can only be inferred by comparison to those of RDX and HMX. SEX appears to be more water soluble than RDX or HMX although no specific numbers are available. Thus SEX would be more available to aquatic life than RDX or HMX and may exhibit a highly toxic effect on the organisms in the Holston River.

Due to the military uniqueness of this compound, it is recommended that the following studies be initiated by the Army.

- Phase II detailed evaluation of the toxicological and environmental hazards of SEX
- solubility studies in water
- further sampling and analysis of SEX at Holston AAP
- the effect on the proposed biotreatment facility be evaluated
- the biotransformation products of SEX in this facility be determined
- *in vitro* mutagenic studies
- acute aquatic toxicity studies
- acute and chronic mammalian toxicity studies

FOREWORD

This report details the results of a preliminary problem definition study on SEX. The purpose of this study was to determine the Army's responsibility for conducting further research on SEX in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on SEX, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

SEX was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

TABLE OF CONTENTS

	<u>Page</u>
Summary.	VI-3
Foreword	VI-5
A. Alternate Names.	VI-9
B. Physical Properties.	VI-9
C. Chemical Properties.	VI-10
1. Synthesis	VI-10
2. General Reactions	VI-10
3. Environmental Reactions	VI-11
4. Sampling and Analysis	VI-12
D. Uses in Army Munitions Production.	VI-12
1. Uses.	VI-12
2. Occurrences of SEX in the Aqueous Effluents from HAAP	VI-12
E. Uses in the Civilian Community	VI-14
F. Comparison of Civilian and Military Uses and Pollution of SEX	VI-14
G. Toxicological and Environmental Hazards.	VI-14
1. Mammalian Toxicity.	VI-14
2. Aquatic Toxicity.	VI-15
3. Availability of Literature for Phase II	VI-15
H. Regulations and Standards.	VI-15
I. Conclusions and Recommendations.	VI-15
J. References	VI-17

LIST OF TABLES

<u>Number</u>		<u>Page</u>
1	Physical Properties of SEX	VI-9
2	Analysis of Waste Streams for RDX, HMX, TAX and SEX.	VI-13

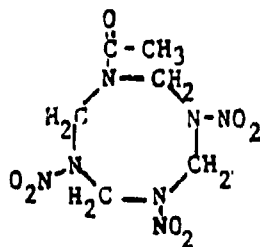
LIST OF FIGURES

<u>Number</u>		<u>Page</u>
1.	Ultraviolet Spectrum of SEX.	VI-10

VI. SEX - OCTAHYDRO-1-ACETYL-3,5,7-TRINITRO-s-TETRAMINE

A. Alternate Names

SEX is a by-product of the RDX/HMX manufacturing process at Holston Army Ammunition Plant (HAAP). This compound has a molecular formula of $C_6H_{11}N_7O_7$ corresponding to the molecular structure shown below:



The molecular weight of SEX is 293.2 g/mole. Pertinent alternate names for SEX are listed below.

CAS Registry No.: unknown

CA Name (9CI): 1,3,5,7-tetrazocine, 1-acetyloctahydro-3,5,7-trinitro

Wiswesser Line Notation:

Synonyms: SEX

B. Physical Properties

Available physical properties of SEX are listed in Table VI-1. The UV absorption spectrum of SEX is shown in Figure VI-1.

Table VI-1. Physical Properties of SEX. *

Physical form @ 20°C:	solid
M.P.:	224.2 - 224.7°C
Solubility:	slightly soluble in pyridine, acetone, and nitromethane. almost insoluble in ethanol, acetic acid, and ethyl ether.

* Reference (Aristoff *et al.*, 1949)

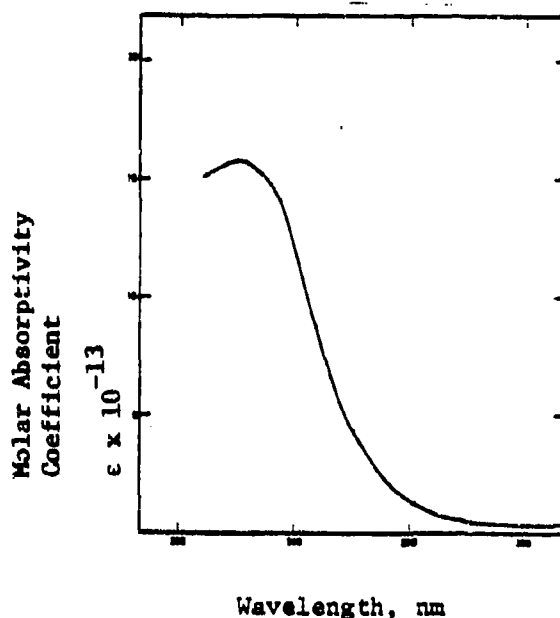


Figure VI-1. Ultraviolet Spectrum of SEX (Schroeder *et al.*, 1951)

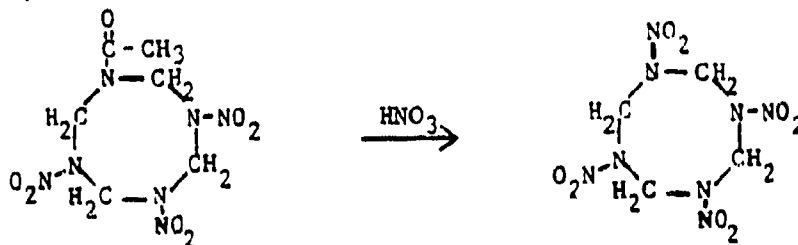
C. Chemical Properties

1. Synthesis

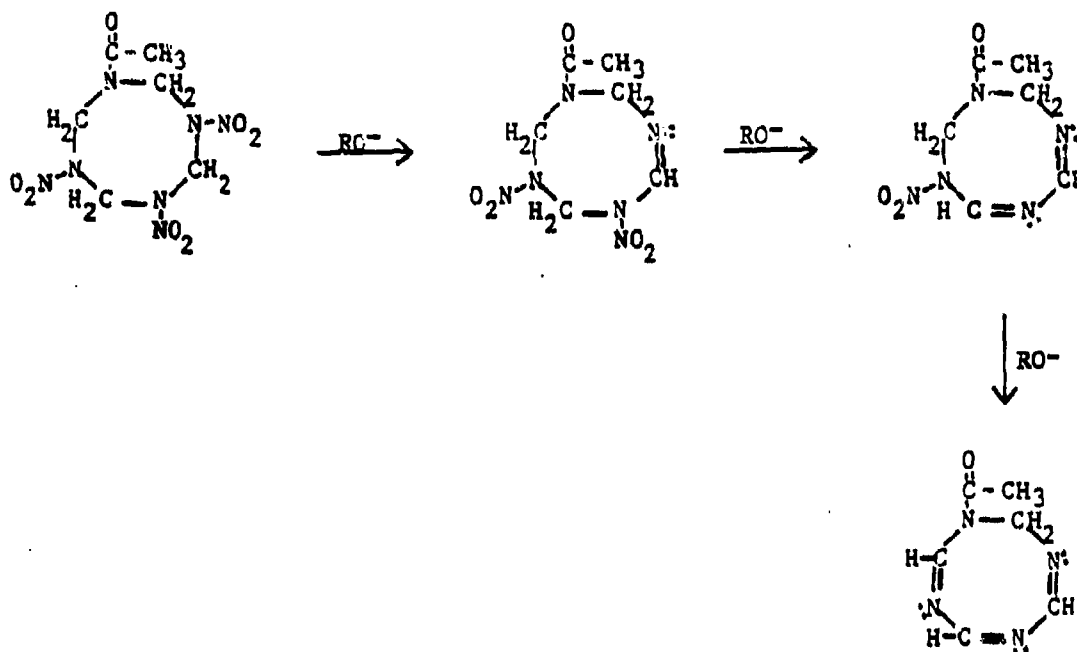
A solution of hexamine in acetic acid was added simultaneously with a solution of ammonium nitrate in nitric acid to acetic anhydride. Following formation of RDX, the solution was diluted with water and filtered. The filtrate was neutralized and stored at 2°C. After five days at 2°C, crude SEX had settled out of solution. The solid was transferred to acetone and boiled. An insoluble residue was obtained. The products were recrystallized repeatedly from acetone and nitromethane to obtain pure SEX (Aristoff *et al.*, 1949)

2. General Reactions

Treatment of SEX with 98% nitric acid at 5°C yields HMX (Aristoff *et al.*, 1949).

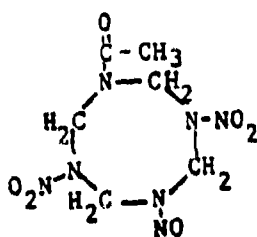


The reaction of secondary nitramines with alkoxide anion has been investigated (Stals, 1969). The base abstracts a methylene proton to form the carbanion which undergoes intramolecular displacement of NO_2^- .

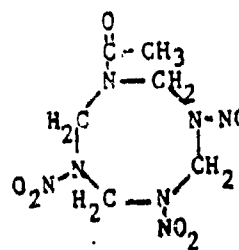


3. Environmental Reactions

The photolysis of dimethylnitramine has been reported (Suryanarayanan and Bulusu, 1970). Irradiation in either ethanol, n-hexane, or acetonitrile yields dimethylnitrosamine. An analogous photodecomposition of SEX would lead to two initial products.

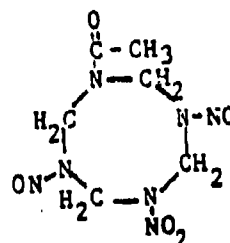
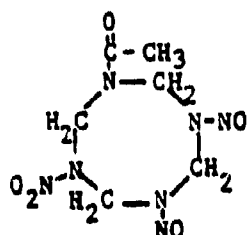


Product 1



Product 2

Prolonged photolysis could lead to two dinitrosamine products.



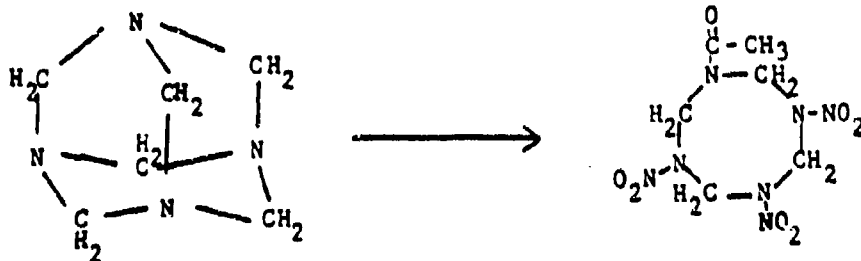
4. Sampling and Analysis

Quantitative analysis of SEX is best performed by instrumental methods. Monitoring for SEX in the wastewater at Holston AAP is accomplished using high pressure liquid chromatography (Holston Defense Corporation, 1978). Samples are obtained by extraction with a methylene chloride:acetonitrile (88:12) mixture. Detection on the level of µg per liter is possible.

D. Uses in Army Munitions Production

1. Uses

SEX is not used or purposely produced by the military. It is an unwanted by-product of RDX/HMX manufacture at Holston Army Ammunition Plant (HAAP). SEX is formed during the nitration of hexamine in the presence of nitric acid/ammonium nitrate and acetic acid/acetic anhydride to produce RDX or HMX. During these processes, some of the hexamine is acetylated by the acetic acid/acetic anhydride solvent.



2. Occurrences of SEX in the Aqueous Effluents from HAAP

In 1977, Holston Defense Corporation began sampling several effluent streams for SEX. The data they obtained depended to a large extent on the manner in which the samples were stored. For comparison purposes, only the analytical results from the samples stored in acetonitrile are presented in Table VI-2. Samples were obtained from four locations:

Table VI-2. Analysis of Waste Streams for RDX, HMX, TAX and SEX
(Holston Defense Corporation, 1978).

Date	Sample Point	RDX	TAX	HMX	SEX
5/17-18/77	N-3	10.0	8.7	2.2	2.2
	N-6	6.3	6.3	1.3	0.2
	T-2	0.2	-	0.04	-
	River	0.07	0.003	-	-
5/24-25/77	N-3	7.2	16.9	2.4	4.0
	N-6	2.2	2.2	1.3	1.0
	T-2	0.4	-	0.6	-
	River	0.007	0.003	0.03	0.001
5/31/77-6/1/77	N-3	2.4	-	4.5	4.8
	N-6	7.0	3.1	2.1	0.6
	T-2	0.4	-	0.07	-
	River	0.006	-	0.006	-
6/6-7/77	N-3	4.3	-	1.5	1.9
	N-6	5.6	5.6	1.7	1.5
	T-2	0.4	0.007	0.1	0.001
	River	0.009	0.003	0.006	0.0007
6/8-9/77	N-3	2.1	2.2	0.3	0.8
	N-6	1.0	1.0	0.4	0.3
	T-2	0.1	0.005	0.03	-
	River	0.0005	0.01	0.0009	-
6/13-14/77	N-3	10.4	5.8	2.9	2.2
	N-6	3.9	0.007	2.4	1.3
	T-2	0.2	0.04	-	-
	River	0.02	0.001	0.01	-
6/17-19/77	N-3	1.8	0.007	4.7	0.5
	N-6	5.3	3.4	2.3	0.7
	T-2	0.3	0.1	-	-
	River	0.02	0.005	0.03	-

- N-3 - manhole below Building N-3 which carries effluents from the G, H, I, J, K, M and N Buildings on lines 1 through 5.
- N-6 - manhole below Building N-6 which carries process effluents from Buildings D6, E6 and G6.
- T-2 - manhole below T-2 (acid area) which carries process effluents from Buildings C3, C5, B9, B11, D3, D5, E3 and E4.
- Holston River at the area B boundary.

From the data in the table, it appears that SEX is entering the environment from the nitration buildings (D-Buildings), the Acids Removal and Explosives Wash (E-Buildings), Recrystallization (G-Buildings), Dewatering (H-Buildings) and the Incorporation Buildings (I, J, K, L, M). However the major amount of SEX entering the environment is from the dewatering and incorporation steps.

Average concentrations of RDX, HMX, TAX and SEX at the four sampling points are given below:

Sample Point	RDX(mg/l)	HMX(mg/l)	TAX(mg/l)	SEX(mg/l)
N-3	5.5	2.6	4.8	2.3
N-6	4.5	1.6	2.6	0.8
T-2	0.3	0.12	0.02	0
River	0.01	0.01	0.004	0

In the effluent from the dewatering and incorporation steps, SEX is present at levels between 50 to 90% of the HMX or 20 to 40% of the RDX present. At full mobilization, ~ 208 million pounds of RDX is produced yearly. If 1% is lost in the effluents, then HAAP could discharge as much as 2.1 million pounds of RDX per year. Discharges of SEX could be 0.4 to 0.8 million lb/year if the 20 to 40% ratio of SEX/RDX is valid.

E. Uses in the Civilian Community

SEX is not used or produced by the civilian community.

F. Comparison of Civilian and Military Uses and Pollution of SEX

SEX is a by-product of the RDX/HMX manufacture at HAAP. There are no civilian uses or products of this chemical. Therefore, SEX is a unique military by-product which enters the environment in the effluents from HAAP.

G. Toxicological and Environmental Hazards

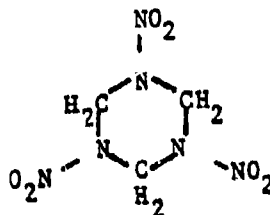
1. Mammalian Toxicity

No mammalian toxicity studies on SEX are reported in the literature. However, its toxicological behaviour is expected to be similar to other nitramines such as RDX. Studies have shown RDX to have a low acute toxicity (Von Ottingen et al., 1949). Chronic exposure by respiratory, gastrointestinal or skin absorption results in nausea, vomiting, convulsions and unconsciousness

in human workers. The American Conference of Governmental Industrial Hygienists (1977) have recommended a TLV of 1.5 mg/m³ for RDX. A similar TLV for SEX would probably provide adequate worker protection.

2. Aquatic Toxicity

Although no aquatic toxicity data on SEX was found in the literature, Liu and Bailey (1977) studied the aquatic toxicity of RDX. RDX is a nitramine having the following structure:



They found a 96 hour LC50 of 5.3 ppm to minnows and a 48 hour EC50 of >41 ppm to *Daphnia magna*. The aquatic toxicity of SEX is probably in this range. Liu and Bailey (1977) also found a low bioaccumulation factor (2 to 3) of RDX. The bioaccumulation of SEX is probably also low. However, at full mobilization the concentration of nitramines (RDX, TAX, HMX and SEX) entering the Holston River would be high enough to cause significant biological stress in areas of the river downstream from HAAP Area B.

Green and Eiklor (1977) found 33% of HMX (an eight member symmetrical nitramine) and 59% of RDX added to a trickling filter were degraded. However the products of this degradation were not identified. It is possible that highly toxic N-nitroso compounds are formed in this degradation.

3. Availability of Literature for Phase II

There appears to be relatively little readily available literature on the toxicity and environmental fate of SEX. However, contacts with foreign RDX manufacturers, evaluation of foreign literature and comparison with other nitramines might prove useful.

H. Regulations and Standards

There are no existing United States regulations or standards for SEX.

I. Conclusions and Recommendations

An evaluation of the readily available literature on SEX has shown it to be a military unique compound. Because of its presence in large quantities in the HAAP effluents, further study of this compound by the Army should be undertaken. The following studies are recommended.

1. Phase II detailed evaluation of the toxicological and environmental hazards of this compound should be undertaken. This study should evaluate the older and the foreign literature on SEX and similar nitramines. Contacts with foreign manufacturers and researchers should also be made.

2. Solubility studies in aqueous media should be conducted if these values are not found in the older literature.

3. Further sampling and analysis of Holston effluents should be undertaken to verify existing data.

4. The effect of SEX on the proposed biotreatment facility as well as its biotransformation products should be determined.

5. Acute aquatic toxicity studies with this compound should be initiated on at least two species present in the Holston River.

6. *In vitro* mutagenic tests should be conducted on SEX.

7. Acute and chronic mammalian toxicity studies should also be conducted by both skin and oral routes of administration.

J. References

- American Conference of Governmental Industrial Hygienists (1977), "Documentation of the Threshold Limit Values for Substances in Workroom Air," 3rd ed.
- Aristoff, E.; Graham, J.A.; Meen, R.H.; Myers, G.S. and Wright, G.F. (1949), "Nitrolysis of Hexamethylenetetramine VI. Recombination of Fragments During Hexamethylenetetramine Nitrolysis in Acetic Anhydride," *Can. J. Res.*, 27B, 520.
- Green, J.M. and Eiklor, J.W. (1977), "Waste Management, Explosives Manufacturing and Finishing, Phase I.," Contract DAAA 09-73-C-0079.
- Holston Defense Corporate (1978), personal communication with R. Jackson and R. Hash.
- Liu, H.W. and Bailey, H.C. (1977), "Toxicity of TNT Wastewater to Aquatic Organisms," Monthly Progress Report No. 27, S.R.I. Project LSU-4262, Contract No. DAMD-17-75-C-5056.
- Schroeder, W.A.; Wilcox, P.E.; Trueblood, K.N. and Dekker, A.O. (1951), "Ultraviolet and Visible Absorption Spectra in Ethyl Alcohol," *Anal. Chem.*, 23(12), 740.
- Stals, J. (1969), "The Chemistry of Aliphatic Unconjugated Nitramines III. Thermal, Electrophilic, and Nucleophilic Reactions," *Australian J. Chem.*, 22, 2515.
- Suryanarayanan, K. and Bulusu, S. (1970), "Photochemical Studies of Secondary Nitramines I. Absorption Spectra of Nitramines and Photolysis of Dimethylnitramine in Solution", AD-712 992.
- Von Oettingen, W.F.; Donahue, D.D.; Yagoda, H.; Monaco, A.R. and Harris, M.R. (1949), "Toxicity and Potential Dangers of Cyclotrimethylene-trinitramine, *J. Ind. Hyg. and Tox.*, 31-21-31, in "Documentation of the Threshold Limit Values for Substances in Workroom Air," 1971, American Conference of Governmental Industrial Hygienists, 3rd. ed.

AD

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

1,3-DINITROBENZENE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAND17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

1,3-DINITROBENZENE

FINAL REPORT

J. P. Kitchens
W. E. Harvard III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

SUMMARY

1,3-dinitrobenzene is not intentionally produced by the Army in its munitions production. This compound is a by-product of TNT manufacture. TNT is manufactured at Radford, Voluntee, Joliet and Newport Army Ammunition Plants. However, there is no current TNT production in the United States.

The toluene starting material used for the manufacture of TNT contains ~250 ppm benzene. In the process, this benzene is nitrated to the dinitro-stage. 1,3-dinitrobenzene accounts for ~93% of the dinitrobenzene formed. Most of the 1,3-dinitrobenzene remains in the final TNT product. However, some portion is discharged in the red water evaporator condensate stream. This stream contains an average of 2 ppm 1,3-dinitrobenzene. Estimated discharges of 1,3-dinitrobenzene from TNT manufacture are between 0.2 and 2.0 lb/line/day. These numbers are dependent on the type of process and the purity of the toluene.

Since 1,3-dinitrobenzene is found in the TNT final product, it can also enter the environment from TNT blending at Holston Army Ammunition Plant and the LAP plants. 1,3-dinitrobenzene can also be produced in the environment by photolysis of 2,4-dinitrotoluene. Once formed, 1,3-dinitrobenzene does not undergo further photochemical decomposition.

There is one civilian manufacturer of 1,3-dinitrobenzene in the United States. All the product produced in the civilian sector is used as a synthetic intermediate, mainly in the dye industry. The pollution from 1,3-dinitrobenzene from the civilian manufacture and use is not known. However, it is probably far less than that from TNT production and use at full mobilization.

1,3-dinitrobenzene is a highly toxic chemical. It can be absorbed through the skin. It produces a variety of symptoms most of which are the result of methemoglobin formation. Because of the toxic nature of 1,3-dinitrobenzene, it has been recommended that women and children under 18 years of age not be allowed around 1,3-dinitrobenzene. This compound is rapidly metabolized by mammals. The methemoglobin formation is believed to be due to the metabolites of 1,3-dinitrobenzene. However, this theory has not been substantiated.

In the aquatic environment, 1,3-dinitrobenzene is toxic to fish and microorganisms. Some soil microorganisms have been shown to degrade 1,3-dinitrobenzene slowly. However, degradation products are nitrosoamines, amines, hydroxylamines, etc. All these compounds are a greater hazard than 1,3-dinitrobenzene itself. Under most circumstances, 1,3-dinitrobenzene will accumulate in the sediment. Some degradation may occur but this degradation will be minor. Bioaccumulation may also occur. However, there are no data on the bioaccumulation factor of 1,3-dinitrobenzene.

In view of the toxicity and the widespread Army pollution of this compound, it is recommended that 1,3-dinitrobenzene be included in the Phase II study. It is also recommended that additional experimental studies be conducted to clarify the environmental fate of 1,3-dinitrobenzene and the

effectiveness of planned treatment processes for removing this compound from effluent streams.

FOREWORD

This report details the results of a preliminary problem definition study on 1,3-dinitrobenzene. The purpose of this study was to determine the Army's responsibility for conducting further research on 1,3-dinitrobenzene in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on 1,3-dinitrobenzene, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

1,3-dinitrobenzene was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition, a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

TABLE OF CONTENTS

	<u>Page</u>
Summary	VII-3
Foreword	VII-5
A. Alternate Names	VII-9
B. Physical Properties	VII-9
C. Chemical Properties	VII-11
1. General Reactions	VII-11
a. Reductive Reactions	VII-11
b. Electrophilic Substitution	VII-12
c. Thermal Decomposition	VII-12
2. Sampling and Analysis	VII-13
D. Uses of 1,3-dinitrobenzene in Army Munitions Production . .	VII-14
1. Purposes	VII-14
2. Speculated or Estimated Losses of 1,3-dinitrobenzene from TNT Manufacturing	VII-14
a. Process Losses	VII-14
b. Production of 1,3-dinitrobenzene in the Environment	VII-15
c. Estimated 1,3-dinitrobenzene Discharges from TNT Manufacture	VII-15
3. Estimated or Speculated Losses from TNT Blending Operations	VII-15
4. Estimated or Speculated Losses from LAP Operations . .	VII-16
E. Uses in the Civilian Community	VII-16
1. Production Methodology	VII-16
2. Manufacturers, Production, and Capacities	VII-16
3. Usages	VII-17
4. Future Trends	VII-16
5. Documented or Speculated Occurrences in the Environment	VII-17
F. Comparison of Military and Civilian Usages of 1,3- dinitrobenzene	VII-17
G. Toxicological and Environmental Hazards	VII-17
1. Human Toxicity	VII-17
2. Toxicity to Mammals and Birds	VII-17
a. Acute and Chronic Toxicity	VII-17
b. Biochemistry	VII-18
c. Mutagenicity, Carcinogenicity and Teratogenicity .	VII-19
3. Toxicity to Aquatic Organisms	VII-18
4. Toxicity to Microorganisms	VII-23
5. Phytotoxicity	VII-23
6. Environmental Fate of 1,3-dinitrobenzene	VII-25
7. Availability of Literature for Phase II	VII-25

Table of Contents
(Continued)

	<u>Page</u>
H. Regulations and Standards	VII-25
I. Conclusions and Recommendations	VII-25
J. References	VII-27

LIST OF TABLES

<u>Number</u>		<u>Page</u>
1	Physical Properties of 1,3-dinitrobenzene	VII-10
2	Estimated Discharges and River Concentrations of 1,3-DNB at Full TNT Production	VII-15
3	Acute Effects of 1,3-dinitrobenzene on Animals	VII-19
4	Metabolites of m-dinitro[¹⁴ C]benzene Excreted in Urine by Rabbits	VII-20
5	Effect of 1,3-dinitrobenzene on Aquatic Organisms	VII-22
6	Growth Inhibition of Bacteria and Fungi by 1,3- dinitrobenzene	VII-24

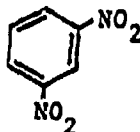
LIST OF FIGURES

<u>Number</u>		<u>Page</u>
1	Infrared Spectrum of 1,3-dinitrobenzene	VII-9
2	1,3-dinitrobenzene Metabolic Pathway in Rabbits	VII-21

VII. 1,3-DINITROBENZENE

A. Alternate Names

1,3-dinitrobenzene is one of the three possible dinitrobenzene isomers. This isomer has the following structure:



The molecular formula of 1,3-dinitrobenzene is $C_6H_4N_2O_4$ corresponding to a molecular weight of 168.11 g/mole. Pertinent alternate names for 1,3-dinitrobenzene are listed below:

CAS Registry No.:	99-65-0
CA Name (9CI):	Benzene, 1,3-dinitro-
CA Name (8CI):	Benzene, m-dinitro-
Wiswesser Line Notations:	WNR CNW
Synonyms:	m-dinitrobenzene; 1,3-dinitrobenzene

B. Physical Properties

The physical properties of 1,3-dinitrobenzene are presented in Table VII-1. The infrared spectrum of this compound is shown in Figure VII-1.

Figure VII-1. Infrared Spectrum of 1,3-dinitrobenzene (Pouchart, 1970).

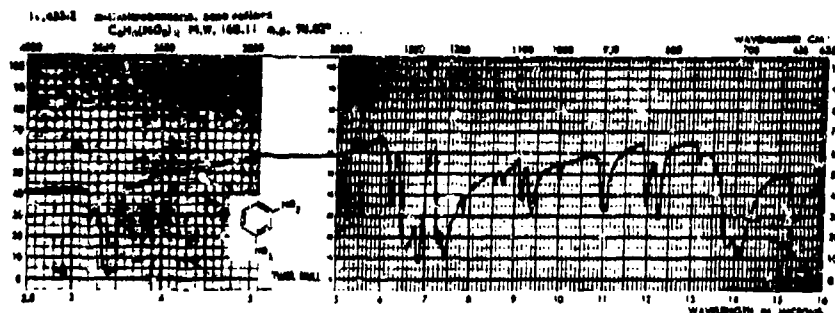


Table VII-1. Physical Properties of 1,3-dinitrobenzene*

Physical Form @ 20°C:	monoclinic needles
Color:	colorless to yellow
M.P.:	89.57°C
B.P.:	302.8°C @ 770 mmHg
	300-303°C @ 760 mmHg
Crystal Density:	d_0^4 1.571
	d_4^{30} 1.5656
Flash Point:	150°C (closed cup)
Heat of Combustion (ΔH_p):	4145 cal/g
Solubility:	water - 0.046 g/100 g @ 15°C
	- 0.32 g/100 g @ 100°C
	ethanol - 2.60 g/100 g @ 20°C
	ethyl ether - 6.7 g/100 g @ 15°C
	benzene - 34.7 g/100 g @ 18°C

*Reference: Kirk and Othmer 1966, 1967; Hawley, 1977;
Windholz, 1976.

The ultraviolet spectrum of 1,3-dinitrobenzene shows an absorption maximum at 233 nm and a corresponding molar absorptivity of 185,000 (CRC, 1974).

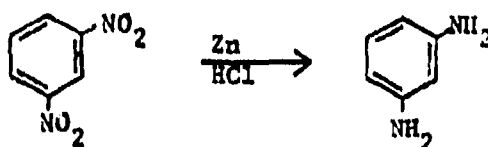
C. Chemical Properties

1. General Reactions

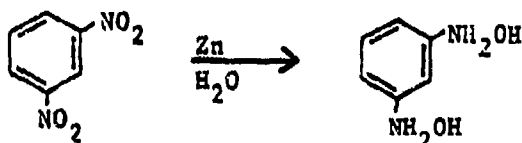
The nitrobenzenes undergo two main types of reactions - reduction and substitution, both electrophilic and nucleophilic.

a. Reductive Reactions

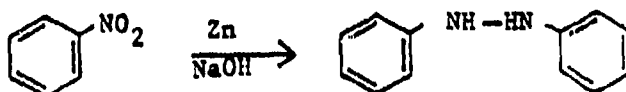
1,3-dinitrobenzene (1,3-DNB) can be reduced to m-phenylenediamine with zinc in HCl, among other reagents.



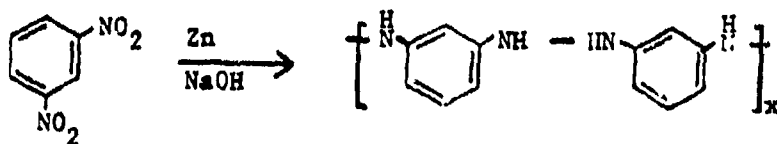
Treatment with Zn in water results in less complete reduction.



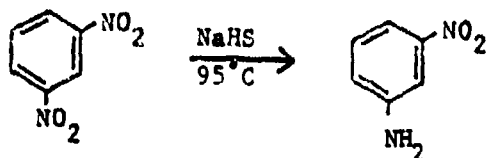
Reduction of mononitrobenzene with Zn in base, or with LiAlH₄ produces N,N'-diphenyl hydrazine (March, 1968).



Reductive coupling of 1,3-DNB may also give a polymeric product of the following structure.

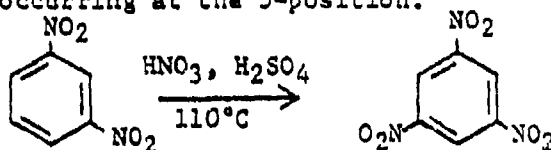


Partial reduction can also be achieved with sulfides. Dinitrobenzene is transformed to m-nitroaniline with NaHS (Abraham, 1968).

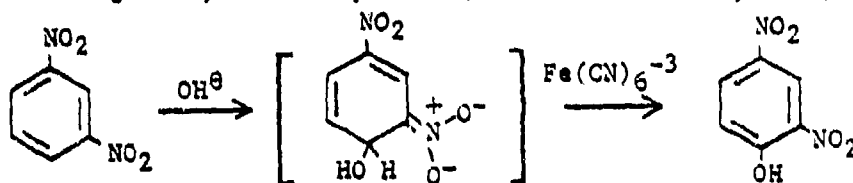


b. Substitution

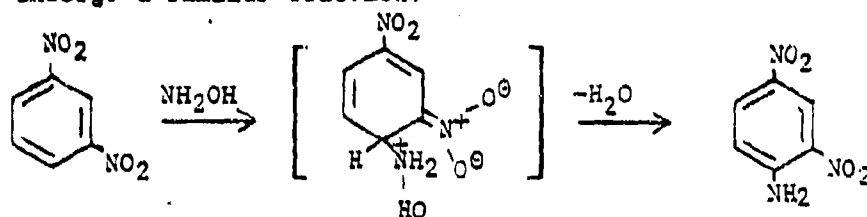
Electrophilic substitutions, normally the most familiar form of aromatic substitutions proceed only with great difficulty. 1,3-dinitrobenzene can be nitrated with anhydrous nitric in fuming sulfuric acids at 110°C (March, 1968). Substitution occurring at the 5-position.



Nitrobenzenes are very susceptible to nucleophilic attack, however, with substitution generally occurring in ortho or para to the nitro groups. 1,3-dinitrobenzene reacts with hydroxyl ion in the presence of oxidizing agents to give 2,4-dinitrophenol (Fieser and Fieser, 1963):



In the absence of an oxidizing agent, azoxybenzenes are obtained in addition to the phenols by disproportionation. 1,3,5-trinitrobenzene reacts with hydroxylamine to form picramide (Fieser and Fieser, 1963). 1,3-dinitrobenzene may undergo a similar reaction:



1,3,5-trinitrobenzene will also undergo nucleophilic addition reactions. For example amines will add to the nitrogen oxygen bonds leading to oxyhydroxylamines (Bernasconi, 1970) and Grignard reagents will attack the aromatic ring leading to substituted cyclohexanes (March, 1968). 1,3-dinitrobenzene might be expected to undergo similar reactions.

c. Thermal Decomposition

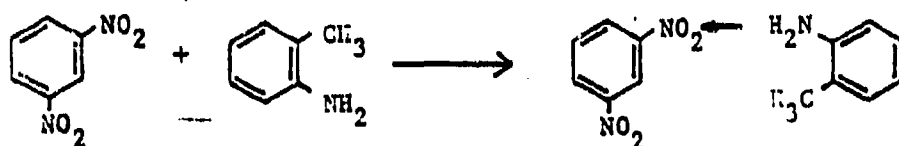
Thermal decomposition of 1,3-DNB can be expected to produce results similar to the decomposition of 1,3,5-TNB. Pyrolysis of 1,3,5-TNB gave a gas mixture containing N_2 , CO , CO_2 , H_2O and small amounts of NO . A multi-component liquid residue and a brown film of nonuniform composition

were also formed. Possible constituents of the liquid are benzene, phenol, aniline, biphenyl, and their nitro and nitroso derivatives. Spectroscopic investigation of the film indicated unsaturated aromatic bonds and the presence of C-NO₂ functional group (Maksimov, 1972).

2. Sampling and Analysis

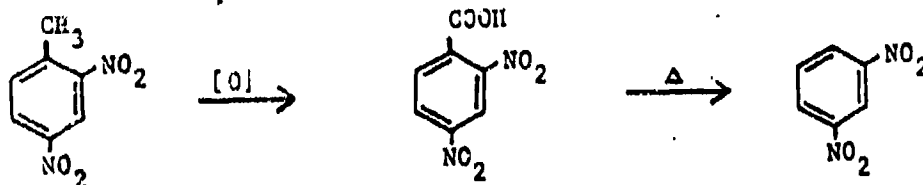
Analytical techniques for 1,3-DNB have been developed in conjunction with the analysis of explosive mixtures. Most of the procedures have been designed to enable analysis in the presence of chemically similar compounds.

Thin layer chromatography (TLC) of dinitrobenzene-amine charge transfer complexes has been used for the separation and identification of explosive components. DNB reacts with an aromatic amine to form a colored charge transfer complex.



Qualitative identification of as little as 2 µg of material in the presence of trinitrotolulene (TNT), trinitrobenzene (TNB), and other aromatic nitro compounds is possible (Parihar *et al.*, 1968).

Gas chromatography (GC) has been used to monitor the composition of the organic phase of a continuous TNT production process (Dalton *et al.*, 1970). GC in tandem with high resolution mass spectrometry has also been used for analysis of TNT impurities (Chang, 1971). Quantitative estimation of DNB may be hindered by the presence of dinitrobenzoic acid (DNBA). DNBA is the oxidation product of dinitrotolulene, a contaminant of TNT resulting from incomplete nitration. High injection port temperatures can yield decarboxylation of the acid, thus raising the apparent 1,3-DNB concentration.



Infrared spectroscopy has been investigated for explosive analysis. It is a dated technique, useful for identification of simple mixtures (Pristera *et al.*, 1960).

D. Uses of 1,3-dinitrobenzene in Army Munitions Production

1. Purposes

The Army does not produce 1,3-dinitrobenzene (1,3-DNB) for use as an explosive. However, under the conditions employed in the production of TNT, the benzene impurities in the toluene starting material are nitrated to dinitrobenzenes. Of the possible dinitrobenzene isomers, 1,3-DNB is ~93% of the product. The benzene impurity in the toluene is nominally present at a 250 mg/l concentration (Kohlbeck and Chandler, 1973). Thus, ~0.017% of the TNT product could be 1,3-DNB.

2. Speculated or Estimated Losses of 1,3-dinitrobenzene from TNT Manufacturing

a. Process Losses

The major 1,3-DNB losses from the TNT manufacturing process occur in the yellow and red water waste streams. The yellow water is either returned to the nitrators or added to the red water. The red water is concentrated in an evaporator. The evaporator condensate is discharged into the environment and is thus the major source of pollutants from the process. The evaporator condensate at VAAP has been shown to contain an average 1,3-DNB concentration of 2.05 mg/l (Barkley, 1978). During this sampling, one continuous line was in operation.

1,3-DNB has not been measured in the effluents from the continuous process at RAAP or JAAP. Since the formation of 1,3-DNB is the result of benzene impurities, the amount discharged would be approximately the same as the VAAP discharges. The Sellite washer flow at RAAP is ~8000 gallons/line/day (Kohlbeck and Chandler, 1973). This water plus the waste yellow water results in a total flow of ~16,000 gallons/line/day. In the evaporator, water is removed until the solids content is 35-40%. Thus, the condensate water released to the environment from continuous lines will be ~11,000 gallons/line/day. The resulting average discharge of 1,3-DNB would be 0.188 lb/line/day at full mobilization for the continuous lines at RAAP, JAAP and VAAP.

The maximum amount of 1,3-DNB which could be produced from one line each day is 17 lb. This number represents a large discrepancy from the sampling data. There are several potential explanations for this discrepancy.

- a large amount of 1,3-DNB is in the final product
- all the benzene present is not nitrated to the dinitrobenzene stage
- reaction losses of 1,3-DNB occur in the process.

There is not sufficient information available to adequately evaluate these

losses. However, a good estimate for all environmental discharges of 1,3-DNB would be between 0.2 lb/line/day and 2.0 lb/line/day. These numbers are highly dependent on the type of process (batch or continuous) and the purity of toluene.

b. Production of 1,3-dinitrobenzene in the Environment

1,3-DNB can be produced photochemically from 2,4-DNT. The amount of 1,3-DNB produced by photoconversion of 2,4-DNT is not known. However, 1% conversion is not an unreasonable number. Discharges of 2,4-DNT at RAAP were reported to be 1.4 lb/day with three lines in operation (Small and Rosenblatt, 1974). At a 1% photoconversion, the resulting 1,3-DNB would be only .005 lb/line/day.

c. Estimated 1,3-dinitrobenzene Discharges from TNT Manufacture

Combining the 1,3-DNB from the process and photochemical sources, discharge rates and river concentrations can be calculated for RAAP, JAAP and VAAP. These data are presented in Table VII-2.

Table VII-2. Estimated Discharges and River Concentrations of 1,3-DNB at Full TNT Production.

Plant	Number of Lines	Total Discharge Rates lb/day	River	River Flow mgd	River Concentration ppb
RAAP	2 continuous	.40	New	2,380	0.02
VAAP	6 batch, 6 continuous	2.4 to 13.2	Tennessee	23,750	0.01 to 0.07
JAAP	3 batch, 6 continuous	1.8 to 7.2	Illinois	5,390	0.04 to 0.16

3. Estimated or Speculated Losses from TNT Blending Operations

TNT is blended with RDX or HMX at Holston AAP. The blending or incorporation operation was described in Section 1.A.1.f., page 40 of this report. 1,3-DNB is not quantitatively measured in the HAAP effluents. Therefore, any discharge values are based on conjecture and should be treated as such.

As discussed earlier, as much as 0.017% of the final TNT product could be 1,3-DNB. At full production, 111 million/lb/year of TNT would be used at HAAP. At full mobilization, an estimated 650 lb/day of TNT would be discharged to the Holston River. 1,3-DNB is approximately twice as soluble as TNT. Using this information, a discharge of from 1.11 to 2.22 lb/day of 1,3-DNB could be expected. The resulting concentration in the Holston River (assuming complete mixing) would be 0.006 to 0.012 ppb.

4. Estimated or Speculated Losses from LAP Operations

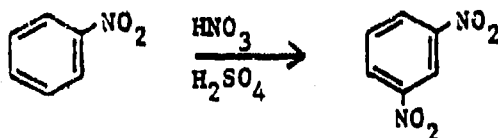
Any 1,3-DNB discharged at the LAP plants would be in the pink water from the melt-pour operations and building wash downs. Cornhusker, Kansas, Lone Star, and Louisiana AAPs dispose of pink water generated from LAP operations by evaporation in ponds or basins. The amount of 1,3-DNB in these evaporation ponds is unknown. The extent of leaching of this compound into the ground water at these facilities is also unknown.

Iowa and Joliet AAPs use carbon adsorption to treat pink water. No detectable 1,3-DNB was found in the effluent from the carbon column at Iowa AAP (Burlinson and Glover, 1976).

E. Uses in the Civilian Community

1. Production Methodology

1,3-DNB is prepared by the mixed-acid nitration of mononitrobenzene.



2. Manufacturers, Production, and Capacities

E. I. duPont is currently the only U.S. manufacturer of 1,3-DNB. They operate a plant of unknown capacity in Deepwater, N. J. 1,3-DNB was previously imported from Germany by the American Hoechst Corporation. They left the market in late 1977.

3. Usages

1,3-DNB is used as a synthetic intermediate. Reduction with aqueous Na₂S at 95°C yields m-nitroaniline, also known as Fast Orange R Base. More complete reduction to m-phenylenediamine is achieved with iron filings in aqueous acid. m-Phenylenediamine is used primarily as a dye intermediate and in the synthetic resin industry. Use of 1,3-DNB as an intermediate reportedly accounts for 100% of the U.S. production.

4. Future Trends

Production of m-phenylenediamine accounts for most of the 1,3-DNB currently made. The phenylenediamine market has been stable for the past ten years showing no appreciable growth or decline (Miller-Stephenson Co., 1978). But OSHA is currently studying m-phenylenediamine along with other industrially used chemicals. If OSHA evaluates m-phenylenediamine unfavorably, a major decline in civilian production can be expected.

Due to the dangers associated with its explosive properties, new uses for m-dinitrobenzene are not actively being investigated.

5. Documented or Speculated Occurrences in the Environment

Occurrences of 1,3-DNB in the civilian environment have not been reported in the literature.

F. Comparison of Military and Civilian Usages of 1,3-dinitrobenzene

Civilian production of 1,3-DNB is small. The exact capacity and current production at the one plant making 1,3-DNB are proprietary. This chemical is used as soon as it is produced for production of dyes. Therefore, the amount of pollution resulting from the civilian production and use of 1,3-DNB would be expected to be minimal. The Army does not intentionally make 1,3-DNB. However, it is present in the pink water effluents, although the amount of this discharge is relatively small.

G. Toxicological and Environmental Hazards

1. Human Toxicity

The toxicity of 1,3-DNB to industrial workers is well documented (Bonzanigo, 1931; Von Oettingen, 1941; Lehky, 1953; Hunter, 1955). Although 1,3-DNB is a solid, it is rapidly absorbed through the skin. Acute symptoms include headache, vomiting, rapid weak pulse, cyanosis and jaundice. Chronic exposure can produce weakness, headache, vomiting, cyanosis and anemia (Fairhall, 1969). Cyanosis or methemoglobinemia occurs when the heme group is oxidized from the Fe^{++} (ferrous state) to the abnormal Fe^{++} (ferric state). The oxygen is tightly bound to the methemoglobin and is not available to the cells. Timar (1947) found that over 60% of the people working in the actual production of TNT had been poisoned. He recommended that women and children under 18 not be allowed to work when 1,3-DNB was present.

Ishikida *et al.* (1976) found a case of 1,3-DNB poisoning due to skin absorption. With the aid of a volunteer they excluded air as the route of exposure and found that 1,3-DNB penetrated supposedly, protective latex gloves. Apparently the effects of 1,3-DNB can vary depending on the individual. Beritic (1956) found 2 women, similarly exposed to 1,3-DNB, with toxic methemoglobinemia. One had liver damage and no Heinz bodies in the erythrocytes, the other woman had Heinz bodies but no liver damage.

Contact by workers with DNB should be limited and their health monitored for possible symptoms. Although DNB is a hazardous substance, removal from exposure will usually relieve the symptoms.

2. Toxicity to Mammals and Birds

a. Acute and Chronic Toxicity

Several studies have been conducted to evaluate the toxicity

of 1,3-DNB. The results of acute toxicity studies on several mammals and birds are presented in Table VII-3. The results of these studies indicate 1,3-DNB to be highly toxic by oral and intravenous administration.

Chronic effects of 1,3-DNB on rats were studied by Christian *et al.* (1975). They administered 1,3-DNB at concentrations of 50, 100 and 200 ppm in the drinking water, over a six week period. The 200 ppm levels were toxic to 2/3 of the male rats. Sublethal effects were noted in both sexes and were related to the level of exposure to 1,3-DNB. These effects were weight loss, atrophy of the testes and deposition of a brown-yellow pigment in the liver cells. In a continuation of this study, more of the sublethal effects were observed on rats with 8 ppm of 1,3-DNB in the drinking water.

Kiese (1949) observed chronic effects of 1,3-DNB in dogs given subcutaneous injections of 0.2-6.0 mg/kg 1,3-DNB. He found a 30% incidence of liver damage and anemia in the dogs. Abood and Romanchek (1957) observed the inhibition of oxidative phosphorylation by rat brain mitochondria following administration of 1,3-DNB. 1,3-DNB partially inhibited succinic dehydrogenase in swine heart muscle (Kadlubow and Kostmatka, 1960). A reduction in the sciatic nerve conduction rate in rats was observed by Pankow *et al.* (1975).

b. Biochemistry

1,3-DNB can enter the body orally, through the lungs or through the skin. Once inside the body, it appears to be rapidly metabolized. Parke (1961) studied the metabolic products of ¹⁴C labeled 1,3-DNB fed to rabbits. The metabolic products he observed and their respective percentage of the dose are given in Table VII-4. The sequence shown in Figure VII-2, is proposed to explain the various metabolites of 1,3-DNB found in these rabbit studies.

The methemoglobinemia caused by 1,3-DNB intoxication is thought to be through its metabolites such as the m-nitrophenylhydroxylamine (Herken, 1944). However, the need for reduction before methemoglobin formation has not been fully substantiated.

c. Mutagenicity, Carcinogenicity and Teratogenicity

Mutagenicity, carcinogenicity and teratogenicity evaluations of 1,3-DNB have not been conducted. However, NCI (1978) has tested m-phenylenediamine (a major metabolite of 1,3-DNB) for carcinogenic potency. This chemical was found to be negative.

3. Toxicity to Aquatic Organisms

Very little information exists on the distribution or levels of 1,3-DNB in the aquatic environment. Laboratory acute toxicity studies have shown that 1,3-DNB is toxic to aquatic organisms. The results of these studies are presented in Table VII-5.

Table VII-3. Acute Effects of 1,3-dinitrobenzene on Animals

Species	Dose (mg/kg)	Route of Adminis.	Effects	Reference
Rats	50	Oral	No mortality produced	Hanavan, 1975
Rats	83	Oral	LD50	Christian <i>et al.</i> , 1975
Dogs	600	Oral	Minimum lethal dose	Von Oettingen, 1941
Dogs	10	i.v.	Serum iron rose sharply after one day and returned to normal in six days	Cammer <i>et al.</i> , 1949
Dogs	10-20	i.v.	Methemoglobinemia, verdoglobulinemia, Heinz bodies, liver damage, cerebral paralysis, convulsions, anemia, increase white cells; LD50 was about 10 mg/kg	Kiese, 1949
Rabbits	400-500	Oral	Minimum lethal dose	Von Oettingen, 1941
Rabbits	200	Dermal	No mortality produced	Hanavan, 1975
Blackbird	42	Oral	LD50	Schafer, 1972
Starling	100	Oral	LD50	Schafer, 1972

Table VII-4. Metabolites of m-dinitro[¹⁴C]benzene Excreted in Urine by Rabbits (Parke, 1961)
m-dinitrobenzene was administered orally as aqueous suspensions. Urines were collected for two days.

Expt. no.	1*	2	3	4	5	6	7	
Dose of m-dinitrobenzene (mg/kg)	100		70	70	60	60	50	50	
Dose of ¹⁴ C (μc/animal)	...	5	4	5	4	4	2	3	Average
Percentage of Dose									
m-dinitrobenzene	0.1	0.3	—	—	2.4	—	0.4	0.7	0.7
m-nitrophenylhydroxylamine	—	—	—	—	—	0.7	1.1	0.75	0.8
m-nitrosodinitrobenzene	—	—	—	—	0.5	0.2	0.1	0.25	0.25
3,3'-dinitroazoxybenzene	—	—	—	—	0.3	0.2	0.3	—	0.3
m-nitroaniline (total)	28	35	10	18	—	—	—	—	—
m-phenylenediamine (total)	<0.2	<0.2	23	25	—	—	—	—	35
2,4-dinitrophenol (total)	0.1	0.1	0.1	—	—	—	—	—	—
2-amino-4-nitrophenol (total)	12.5	15	12	16	—	—	—	—	—
4-amino-2-nitrophenol (total)	1.4	1.6	2.1	2.6	—	—	—	—	0.1
2,4-diaminophenol (total)	19	37	38	28	—	—	1.9	2.4	14
Total metabolites							(0.6)*	(1.0)*	2.0
Total radioactivity in urine	61	89	85	93	—	—	—	—	(0.8)*
Total radioactivity in feces	65	89	82	93	71	89	75	83	81
	—	0.3	1.0	—	5.2	—	—	—	—

*Estimated after enzymatic hydrolysis

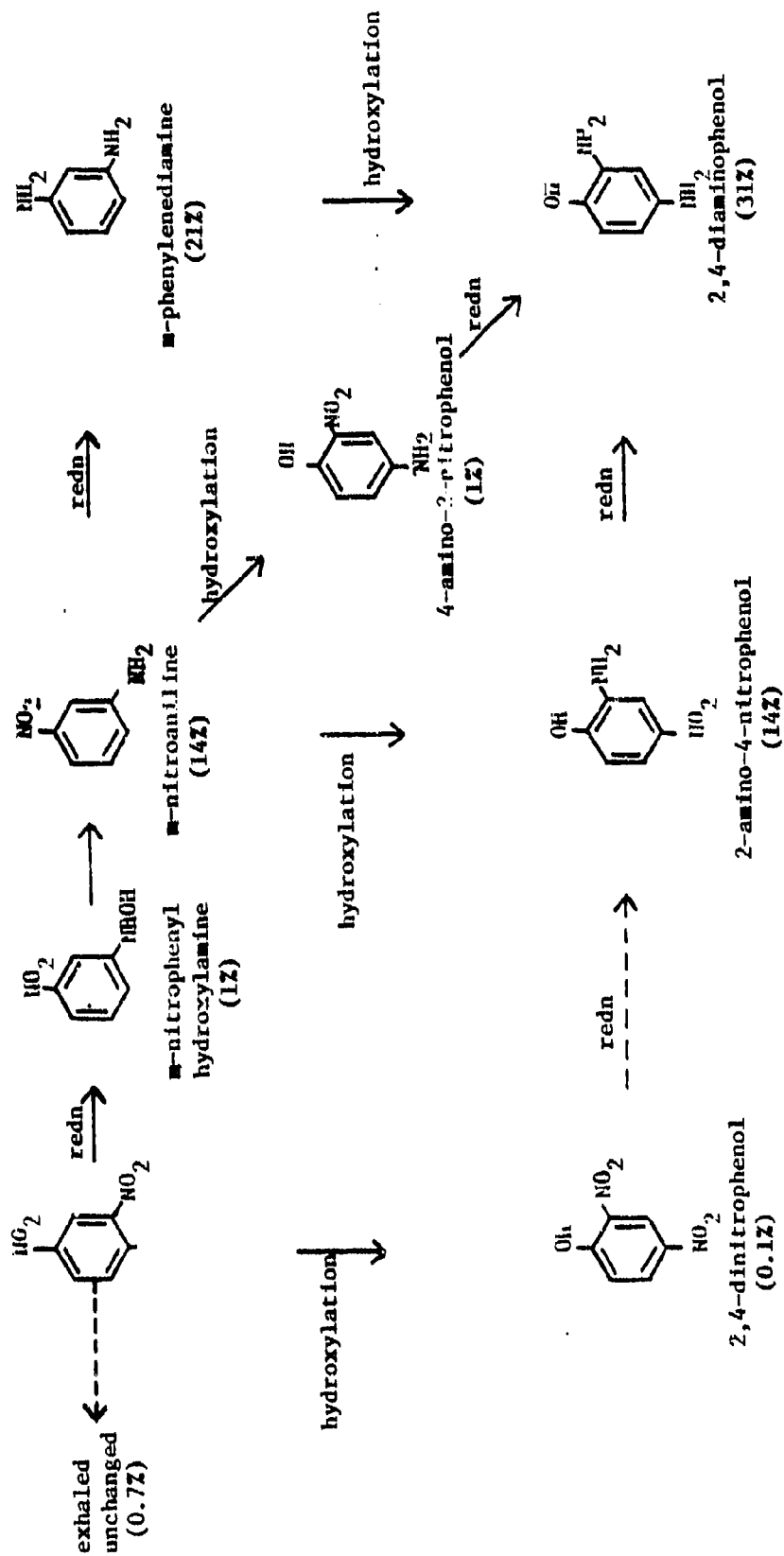


Figure VII-2. 1,3-dinitrobenzene Metabolic Pathway in Rabbits (Parke, 1961).

Table VII-5. Effect of 1,3-dinitrobenzene on Aquatic Organisms.

Species	Conc.	Water	Temp °C	Effect	Reference
Minnow (<i>Phoxinus laevis</i>)	10-12 8-10	distilled hard	23 23	6-hr lethal threshold 6-hr lethal threshold	LeClerc, 1960 LeClerc, 1960
Fathead minnow (<i>Pimephales promelas</i>)	7.4	soft	20	96-hr LC50	Liu and Bailey, 1977
Water flea (<i>Daphnia magna</i>)	53.0	soft	20	48-hr LC50	Liu and Bailey, 1977

4. Toxicity to Microorganisms

Several studies are published which describe the action of 1,3-DNB on various bacteria and fungi. 1,3-DNB has been shown to inhibit the growth of many bacteria and fungi at relatively low concentrations. These inhibitory effects are summarized in Table VII-6. Chambers *et al.*, (1963) found a relatively low oxygen uptake and slow oxidation of 1,3-DNB by several microorganisms (predominantly *Pseudomonas*). Growth inhibition of young colonies of *Aspergillus niger* was observed by Higgins (1960). His observations indicated a depression in amino acid synthesis through the formation of citric acid cycle intermediate in the early growth phase. In mature cultures, the 1,3-DNB metabolism was a sulfhydryl dependent, pyridine nucleotide-linked ferro-flavoprotein.

In spite of its growth inhibitory effects on most microorganisms, there are a few species capable of metabolizing 1,3-DNB. Soil microorganisms degrade 1,3-DNB slowly with degradation times of 64 days (Alexander and Lustigman, 1966). Bringman and Kuhn (1971) developed a two stage aerated process for degradation of 1,3-DNB. The first stage contained *Azobacter agilis* and the second stage, activated sludge. After 36 hours, 95-97% of the 1,3-DNB was reduced.

The mechanism of biodegradation of 1,3-DNB is thought to be a reductive process. This process proceeds along the following steps:



m-nitronitrosobenzene was identified as a 1,3-DNB metabolite from *Proteus vulgaris* (Hartwig and Lipschitz, 1920). m-nitronitrosobenzene and m-nitrophenylhydroxylamine have been identified as metabolites from American baker's yeast (Creach, 1936). Thus, the metabolites of 1,3-DNB such as

- m-nitronitrosobenzene
- m-nitrophenylhydroxylamine
- m-nitroaniline
- m-phenylenediamine

could present a greater hazard to the environment than the 1,3-DNB itself.

5. Phytotoxicity

The affect of 1,3-DNB on the photosynthesis of *Chlorella* and spinach chloroplast was examined. The photochemical and thermal phases of fluorescence induction were inhibited by 1,3-DNB. The data suggests an irreversible binding of 1,3-DNB to the reaction centers. Thus, 1,3-DNB may adversely affect plants by interference with the photosynthetic process (Howard *et al.*, 1976). The inhibiting growth action of nitrated benzene was reported by Stom and Khutorianskii (1972). The inhibitory action was found to be directly related to the electron acceptor ability of the molecule.

Table VII-6. Growth Inhibition of Bacteria and Fungi by 1,3-dinitrobenzene.

Species	Conc. mg/l	Medium	Effect	Reference
Bacteria				
<i>Streptococcus</i> sp.	33	---	inhibition	Lecoq and Landrin (1951)
Human tuberculin bacillus	5	---	"	" " "
Fungi				
<i>Aspergillus niger</i>	4	glucose	complete inhibition	Higgins (1958)
"	0.4	"	no inhibition	" "
"	40	serum-mash	complete inhibition	Zsolnai (1961)
<i>Penicillium simplicissimum</i>	40	"	"	" "
<i>Tricothecium roseum</i>	100	"	"	" "
<i>Candida albicans</i>	200	"	partial inhibition	" "
<i>Achorion quinqueangulum</i>	100	"	complete inhibition	" "
<i>Trichophyton gypsum</i>	100	"	"	" "
<i>Epidermophyton Kaufman-Wolf</i>	100	"	"	" "

In contrast, McRae (1970) reported almost total herbicidal effects of 2 lb/acre of 1,3-DNB with no crop phytotoxic response. The exception was tomatoes.

6. Environmental Fate of 1,3-dinitrobenzene

1,3-DNB has been shown to be photochemically stable under environmental conditions (Barkley, 1978). Losses of 1,3-DNB from water due to volatility are expected to occur. Due to its low solubility, 1,3-DNB would be expected to concentrate in the sediment.

Biodegradation is expected to occur only slowly in the environment. The resulting metabolites may be more hazardous than the 1,3-DNB itself. Bioconcentration factor for 1,3-DNB has been calculated based on its octanol/water partition coefficient. This factor is 8.53 (Howard *et al.*, 1976). This factor is very low when compared to such chemicals as endrin which has a factor of 2957±10 (Howard, *et al.*, 1976). A significant amount bioconcentration of 1,3-DNB would not be expected to occur. Thus, 1,3-DNB could present a long term chronic toxicity problem in the environment.

7. Availability of Literature for Phase II

1,3-DNB has been widely studied. Research on toxicological properties of this compound are reported in both the United States and foreign literature. Therefore, sufficient literature is available for a detailed Phase II evaluation.

H. Regulations and Standards

1. Air and Water Regulation

1,3-DNB is a small volume chemical and is not specifically regulated by air or water effluent guidelines. However, this compound is listed in the Toxic Substances Control Act Candidate List of Chemicals (EPA, 1977).

2. Human Exposure Standards

The American Conference of Governmental Industrial Hygienists (1977) recommends a skin exposure TLV of 1 mg/m³. This value has been adopted by OSHA (1974). 1,3-DNB is not on the list of chemicals to be evaluated for carcinogenic potential by NCI in their bioassay program.

I. Conclusions and Recommendations

1,3-DNB is not a military unique compound. However, pollution from this compound by the military is at least as high as that from civilian production and usage. The military pollution is also widespread, occurring in the effluents from TNT manufacturing, blending and loading facilities and from the photodecomposition of 2,4-DNT in these effluents.

1,3-DNB is highly toxic to mammals, aquatic organisms and microorganisms. No photodegradation in the aqueous environment occurs and microbial degradation occurs slowly. In addition, microbial degradation can lead to toxic N-nitroso and amine compounds.

After evaluation of this data and taking into consideration the possible decline in civilian production and use, it is recommended that the Army initiate additional work on this compound. This work should include

1. A phase II detailed toxicological and environmental evaluation
2. Bioaccumulation studies
3. The effects of this compound on effluent treatment facilities
 - a) ability of the biotreatment facilities at Holston AAP to degrade this compound and identification of the degradation products
 - b) the effect of this compound on the carbon adsorption columns and the ability of the carbon to effectively remove it from the effluent
4. Further quantitation of the actual amount of 1,3-DNB in the TNT final product
5. Quantitation of the photochemical formulation of the 1,3-DNB from TNT and DNT waste waters.

J. References

- Abood, L. and Romanchek, L. (1957), "The Chemical Constitution and Biochemical Effects of Psychotherapeutic and Structurally Related Agents," *Ann. N.Y. Acad. Sci.*, 66, 812, in Chem. Abstr. 51:14782g.
- Abraham, E.N. (1968), *Dyes and Their Intermediates*, Pergamon Press, New York.
- Alexander, M. and Lustigman, B. (1966), "Effect of Chemical Structure on Microbial Degradation of Substituted Benzenes," *J. Agr. Food Chem.*, 14, 410.
- American Conference of Governmental Industrial Hygienists (1977), *Documentation of the Threshold Limit Values for Substances in Workroom Air*, 3rd. ed.
- Barkley, J.J. (1978), "Condensate Water Compounds," memorandum to J. Gareth Pearson.
- Beritić, T. (1956), "Two Cases of *m*-dinitrobenzene Poisoning with Unequal Clinical Response," *Brit. J. Ind. Med.*, 13, 114, from Chem Abstr. 13:17185.
- Bernasconi, C.F. (1970), "Intermediates in Nucleophilic Aromatic Substitution," *J. Amer. Chem. Soc.*, 92, 129, 4688.
- Bonzanigo, A. (1931), "Industrial Poisoning with Aniline and Similar Substances," *Deut. Z. Ges. Gericht. Med.*, 16, 242, from Chem. Abstr. 25:2214.
- Bringmann, G. and Kuhn, R. (1971), "Biological Decomposition of Nitrotoluenes and Nitrobenzenes by *Azobacter agilis*," *Gesundh.-Ing.*, 92(9), 273.
- Burlinson, N.E. and Glover, D.J. (1976), "Photochemistry of TNT and Related Nitroaromatics - Investigation of the Pink Water Problem," Quarterly Progress Report No. 8, MIPA 6968.
- Cammer, A.; Kiese, M. and Tauschwitz, K. (1949), "Pharmacological Investigations of *m*-dinitrobenzene. II. Iron Metabolism in Acute *m*-dinitrobenzene Poisoning," *Arch. Exptl. Path. Pharmacol.*, 206, 384.
- Chambers, C.; Tabak, H. and Kabler, P. (1963), "Degradation of Aromatic Compounds by Phenol-adapted Bacteria," *J. Water Poll. Control Fed.*, 35, 1517 in Howard *et al.* (1976), "Investigation of Selected Potential Environmental Contaminants: Nitroaromatics," EPA Contract No. 68-01-2999.
- Chang, T.L. (1971), "Identification of Impurities in Crude TNT by Tandem GC-MS Technique," *Anal. Chim. Acta.*, 53, 445.
- Christian, R.I. *et al.* (1975), "The Development of a Test for the Potability of Water Treated by a Direct Reuse System," Annual Summary Report, Contract No. DADA-17-73-C-3013.
- CRC (1974), *Spectral Data and Physical Properties of Chemical Compounds*, 2nd ed., Chemical Rubber Co., Cleveland, Ohio, 1-VII.

- Creach, P. (1936), "Action of Metadinitrobenzene on the Metabolism of American Baker's Yeast (Fleischman's)," *Comp. Rend. Soc. Biol.*, 121, 246.
- Dalton, R.W.; Kohlbeck, J.A. and Bolleter, W.R. (1970), "Gas Chromatographic Analysis of Trinitrotoluene from the Continuous Process," *J. Chromatogr.*, 50, 219.
- EPA (1977), Toxic Substances Control Act Candidate List of Chemical Substances, PL 94-469.
- Fairhall, L. (1969), *Industrial Toxicology*, Hafner Publ. Co., N.Y., 227.
- Fieser, L.F. and Fieser, M. (1961), *Advanced Organic Chemistry*, Reinhold Publishing Corp., New York.
- Hanavan (1975), in Howard, P.; Santodonato, J.; Saxena, J.; Malling, J. and Greninger, D. (1976), "Investigation of Selected Potential Environmental Contaminants: Nitroaromatics," EPA Contract No. 68-01-299.
- Hawley, G.C. (1977), *The Condensed Chemical Dictionary*, 9th ed., Van Nostrand and Reinhold Co., N.Y.
- Herten, H. (1944), "Methemoglobin Formation. XXVII. Some Aromatic Nitro Derivatives," *Arch. Exptl. Path. Pharmacol.*, 202, 70, from Chem. Abstr. 33:1561.
- Hartwig, G. and Lipschitz, W. (1920), "Mechanism of the Toxic Action of Aromatic Nitro Compounds," *Arch. Ges. Physiol.*, 183, 275, in Chem. Abstr. 15, 708.
- Higgins, E. (1958), "Inhibition of *Aspergillus niger* Growth by *m*-dinitrobenzene and Its Reversal by Amino Acids," *Proc. Soc. Exptl. Biol. Med.*, 99, 527.
- Higgins, E. (1960), "Metabolic Effects of *m*-dinitrobenzene in *Aspergillus niger*," *Proc. Soc. Exptl. Biol. Med.*, 105, 583.
- Higgins, E. (1961), "Nitroaryl Reductase of *Aspergillus niger*," *Enzymologia*, 23(3), 176.
- Howard, P.; Santodonato, J.; Saxena, J.; Malling, J. and Greninger, D. (1976), "Investigation of Selected Potential Environmental Contaminants: Nitroaromatics," EPA Contract No. 68-01-2999.
- Hunter, D. (1935), "The Disease of Occupations," Little, Brown and Co., Boston in Howard *et al.* (1976), "Investigation of Selected Potential Environmental Contaminants: Nitroaromatics," EPA Contract No. 68-01-2999.
- Ishihara, N.; Kanaya, A. and Ikeda, M. (1976), "*m*-dinitrobenzene Intoxication Due to Skin Absorption," *Int. Arch. Occup. Environ. Hlth.*, 36, 161.
- Kadlubow, R. and Kostmatka, S. (1960), "The Effect of Aromatic Nitro and Amino Compounds on the Activity of Succinic Dehydrogenase," *Med. Pracy.*, 11, 247.

- Kiese, M. (1949), "Pharmatologische Untersuchungen uber m-dinitrobenzol. II. Mitteilung Chronische Vergiftung mit m-dinitrobenzol," *Arch. Pharmak.*, 206, 505 in Howard *et al.* (1976), "Investigation of Selected Potential Environmental Contaminants: Nitroaromatics," EPA Contract No. 68-01-2999.
- Kirk, R. and Othmer, D. (1966), *Encyclopedia of Chemical Technology*, The Interscience Encyclopedia, Inc, N.Y., 9, 392.
- Kirk, R. and Othmer, D. (1967), *Encyclopedia of Chemical Technology*, The Interscience Encyclopedia, Inc, N.Y., 13
- Kohlbeck, J.A. and Chandler, C.D., Jr. (1973), "Continuous TNT Characterization Study (PE-238); Continuous TNT Process Control and Characterization Study - Extension (PE-289)" in Howard *et al.* (1976), "Investigation of Selected Potential Environmental Contaminants: Nitroaromatics," EPA Contract No. 68-01-2999.
- LaClere, E. (1960), "The Self-Purification of Streams and the Relationship Between Chemicals and Biological Tests," *Proc. 2nd Symp. on Treatment of Waste Waters*, 281.
- Lecoq, R. and Landrin, P. (1951), "Importance of the Position and Mobility of Nitrogroups on the Antibiotic Action of Benzene Derivatives," *Compt. rend.*, 232, 762, in Chem. Abstr. (1942) 16701.
- Lehky, B. (1953), "Case of Collective Poisoning with m-dinitrobenzene," *Pracovní Lékařství.*, 5, 219, in Chem. Abstr. V2:3445f.
- Liu, D. and Bailey, H.C. (1977), "Toxicity of TNT Wastewater to Aquatic Organisms," Monthly Progress, Report No. 27.
- Maskimov, Y.Y. (1972), "Thermal Decomposition of Aromatic Polynitro Compounds in Vapors," *Zh. Fiz., Khim.*, 46(7), 1726.
- March, J. (1968), *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, McGraw-Hill, New York.
- McRae, Dougal H. (1970), "Herbicidal m-dinitrobenzene," *Ger. Offen.*, 29, in Chem. Abstracts 77:15616u.
- Miller-Stephenson Co., (1978) personal communication.
- NCI (1978), "Chemicals Being Tested for Carcinogenicity by the Bioassay Program, DCCP, NCI," Feb., 1978.
- OSHA (1974), *Federal Register*, 39, 23540.
- Pankow, D.; Glatzel, W.; Tietze, K. and Ponsold, W. (1975), "Motor Nerve Conduction Velocity after Carbon Monoxide or m-Dinitrobenzene Poisoning Following Elimination of the Poisons," *Arch. Toxicol.*, 34, 325.

- Parihar, D.B.; Sharma, S.P. and Verma, K.K. (1968). "Trace Analysis of Explosives as Pt Complexes," *J. Forensic Sci.*, 13, 246.
- Parke, D. (1961), "Studies in Detoxification V. The Metabolism of m-Dinitro [¹⁴C] Benzene in the Rabbit," *Biochem. J.*, 78, 262.
- Priesters, F.; Halik, M.; Casanli, A. and Fredericks, W. (1960), "Analysis of Explosives using Infrared Spectroscopy," *Anal. Chem.*, 32, 495 in Howard et al. (1976), "Investigation of Selected Potential Environmental Contaminants: Nitroaromatics," EPA Contract No. 68-01-2999.
- Pouchert, Charles J. (1970), *The Aldrich Library of Infrared Spectra*, Aldrich Chemical Co., Inc., U.S.A.
- Schafer, E. (1972), "The Acute Oral Toxicity of 369 Pesticidal, Pharmaceutical and other Chemicals to Wild Birds," *Toxicology and Applied Pharmacology*, 21, 315.
- Small, M.J. and Rosenblatt, D.H. (1974), "Munitions Production Products of Potential Concern as Waterborne Pollutants - Phase II," Technical Report 7404, United States Army Medical Research and Development Command.
- Stom, D.I. and Khutorianskii, V.A. (1972), "Inhibitory Activity of Aromatic Compounds and Their Electron-Acceptor Ability," *Fiziol. Biokhim. Kul't. Rast.*, 4(2), 183.
- Timar, M. (1947), "Industrial Poisoning in the Manufacture of Explosives," *Orvosok Lapja es Nepesesszegugy.* 3, 252, from Chem Abstr. 43:8681c.
- Von Oettinger, W. (1941), Public Health Bulletin 271, Washington, D.C., in EPA (1976), Quality Criteria for Water.
- Windholz, M. (1976), *The Merck Index*, 9th ed., Merck and Co., Inc. Rahway, New Jersey.
- Zsolnai, T. (1961), "Versuche zur Entdeckung neuer Fungistatika II. Nitroverbindungen," *Biochemical Pharm.*, 5, 287.

AD

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

1,3,5-TRINITROBENZENE

FINAL REPORT

J. F. Kitchens
W. E. Harward III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7057

COTR: Clarence Wada, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

AD

PRELIMINARY PROBLEM DEFINITION STUDY OF
48 MUNITIONS-RELATED CHEMICALS

VOLUME I EXPLOSIVES RELATED CHEMICALS

1,3,5-TRINITROBENZENE

FINAL REPORT

J. F. Kitchens
W. E. Harvard III
D. M. Lauter
R. S. Wentzel
R. S. Valentine

April 1978

Supported by:

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, Maryland 21701

Contract No. DAMD17-77-C-7957

COTR: Clarence Wade, Ph.D.

ATLANTIC RESEARCH CORPORATION
Alexandria, Virginia 22314

Approved for Public Release
Distribution Unlimited

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

SUMMARY

1,3,5-trinitrobenzene is an explosive not manufactured by either the civilian or military communities. It is, however, a by-product in the manufacture of TNT. TNT manufacturing facilities are located at Radford AAP, Volunteer AAP, Joliet AAP and Newport AAP. However, no TNT is currently being produced in the United States. During the nitration of toluene competitive oxidation of TNT to 2,4,6-trinitrobenzoic acid occurs. This acid is then decarboxylated in the nitrator or Sellite washers to 1,3,5-trinitrobenzene. Most of the trinitrobenzene formed is found in the final TNT product. However, small amounts are discharged in the evaporator condensate from the evaporation of red water. Estimates of the 1,3,5-trinitrobenzene discharges from the manufacture of TNT are 0.39 lb/line/day.

Since 1,3,5-trinitrobenzene is formed in concentrations of 0.1 to 0.7% of the TNT product, it can also be found in effluent from blending operations at Holston AAP and loading (LAP) at Joliet AAP, Cornhusker, Kansas, Lone Star, Louisiana and Iowa AAPs. Estimated discharges from blending operations at Holston could be as much as 9 lb/day. The discharges from the LAP facilities vary depending on how the pink water is handled. Cornhusker, Kansas, Lone Star and Louisiana dispose of pink water in evaporation ponds. Joliet and Iowa have carbon adsorption columns.

In addition to the 1,3,5-trinitrobenzene in the effluent from the manufacture, blending and loading of TNT, 1,3,5-trinitrobenzene is formed photochemically from TNT in the waste water. It is estimated that 1% of the TNT discharged is converted to 1,3,5-trinitrobenzene. This compound is not further photochemically degraded.

1,3,5-trinitrobenzene is moderately toxic in acute doses. It is, however, very toxic in subacute or chronic doses. The main biochemical activity of this compound is the formation of methemoglobin.

In the environment, 1,3,5-trinitrobenzene is toxic to aquatic organisms. It can be degraded by microorganisms but only with difficulty. Environmental reactions such as complexation and derivatization can occur. However, it appears that 1,3,5-trinitrobenzene tends to concentrate in the sediments and bioaccumulate in aquatic organisms.

1,3,5-trinitrobenzene is a unique military chemical. Some minor pollution may occur from civilian manufacture of nitrated aromatics. However, the military pollution arising from this compound in the process effluents and from photodecomposition of TNT in the environment is the major source of 1,3,5-trinitrobenzene in the environment.

The following recommendations are made for 1,3,5-trinitrobenzene:

- Phase II study be initiated
- additional sampling at RAAP or VAAP (when operational) and HAAP be carried out to determine the extent of sediment and biological accumulation

- studies be conducted on the removal of 1,3,5-trinitrobenzene by carbon adsorption and its affect on the bed to volume breakthrough for TNT and RDX
- studies be conducted to determine the biodegradation products of 1,3,5-trinitrobenzene.

FOREWORD

This report details the results of a preliminary problem definition study on 1,3,5-trinitrobenzene. The purpose of this study was to determine the Army's responsibility for conducting further research on 1,3,5-trinitrobenzene in order to determine its toxicological and environmental hazards so that effluent standards can be recommended. In order to determine the Army's responsibility for further work on 1,3,5-trinitrobenzene, the military and civilian usage and pollution of this chemical were evaluated. In addition, a preliminary overview of toxicological and environmental hazards was conducted.

1,3,5-trinitrobenzene was only one of 48 chemicals evaluated under Phase IA of contract No. DAMD17-77-C-7057. These chemicals are grouped in four categories

- explosives related chemicals
- propellant related chemicals
- pyrotechnics
- primers and tracers

Each category is a major report. Section I of each report is an overview of the military processes which use each chemical and the pollution resulting from the use of these chemicals. The problem definition study reports on each chemical are separable sections of these four reports.

In addition a general methodology report was also prepared. This report describes the search strategy and evaluation methodology utilized for this study.

TABLE OF CONTENTS

	<u>Page</u>
Summary	VIII-3
Foreword	VIII-5
A. Alternate Names	VIII-9
B. Physical Properties	VIII-9
C. Chemical Properties	VIII-9
1. General Reactions	VIII-9
2. Sampling and Analysis	VIII-13
D. Uses of 1,3,5-trinitrobenzene in Army Munitions Production	VIII-14
1. Purposes	VIII-14
2. Estimated or Speculated Losses of 1,3,5-TNB from TNT Manufacture	VIII-14
a. Process Losses	VIII-14
b. 1,3,5-TNB Production in the Environment	VIII-15
c. Estimated 1,3,5-TNB Discharges from TNT Manufacture	VIII-16
3. Estimated or Speculated Losses of 1,3,5-TNB from TNT Blending	VIII-16
4. Estimated or Speculated Losses of 1,3,5-TNB from LAP Operations	VIII-16
E. Uses of 1,3,5-trinitrobenzene in Civilian Community	VIII-17
1. Production Methodology	VIII-17
2. Manufacturers, Production, and Capacities	VIII-17
3. Usages	VIII-17
4. Future Trends	VIII-18
5. Documented or Speculated Occurrences in the Environment	VIII-18
F. Comparison of Army and Civilian Uses of 1,3,5-TNB	VIII-18
G. Toxicological and Environmental Hazards of 1,3,5- trinitrobenzene	VIII-18
1. Mammalian Toxicity	VIII-18
2. Aquatic Toxicity	VIII-20
3. Microorganism Toxicity	VIII-20
4. Phytotoxicity	VIII-22
5. Environmental Fate	VIII-22
6. Availability of Literature for Phase II	VIII-23
H. Regulations and Standards	VIII-23
I. Conclusions and Recommendations	VIII-23
J. References	VIII-25

Table of Contents
(Continued)

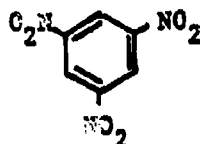
LIST OF TABLES

<u>Number</u>		<u>Page</u>
1	Physical Properties of 1,3,5-trinitrobenzene	VIII-10
2	Estimated Discharges and River Concentrations of 1,3,5-TNB at Full TNT Production	VIII-16
3	Acute and Chronic Animal Toxicity of 1,3,5-trinitrobenzene	VIII-19
4	Effect of 1,3,5-trinitrobenzene on Aquatic Organisms . . .	VIII-20
5	Growth Inhibition of Bacteria and Fungi by 1,3,5-TNB . . .	VIII-21
6	Concentration of Nitrobenzenes Required for 50% Inhibition of Growth Rate of <i>Trichoderma viride</i>	VIII-22

VIII. 1,3,5-TRINITROBENZENE

A. Alternate Names

1,3,5-trinitrobenzene is an explosive having the following chemical structure:



It has a molecular formula of $C_6H_3N_3O_6$ and a corresponding molecular weight of 213.11 g/mole. Pertinent alternate names for 1,3,5-trinitrobenzene are listed below:

CAS Registry No.:	99-35-4
CA Name (8 CI):	benzene, 1,3,5-trinitro-
Wiswesser Line Notation:	WNR CNW ENW
Synonyms:	Benzite; s-trinitrobenzene; sym-trinitrobenzene; symmetric-trinitrobenzene; TNB; Trinitrobenzene; 1,3,5-trinitrobenzene

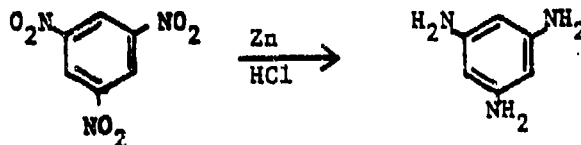
B. Physical Properties

The physical properties of 1,3,5-trinitrobenzene are presented in Table VIII-1. The ultraviolet spectrum of 1,3,5-trinitrobenzene has an adsorption maximum at 226 mμ with a molar absorptivity of 26,915 (CRC, 1974).

C. Chemical Properties

1. General Reactions

1,3,5-trinitrobenzene (1,3,5-TNB) can be reduced to triamino-benzene with zinc in HCl, among other reagents.



Treatment with Zn in water results in less complete reduction.

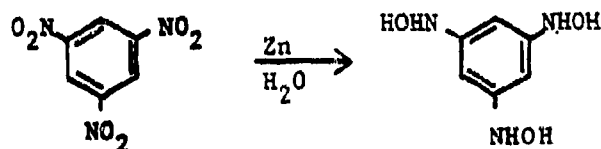
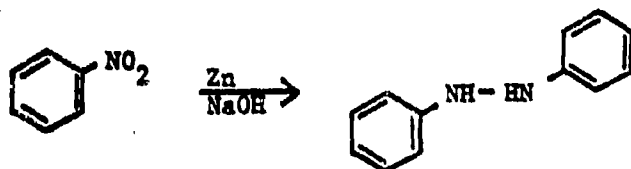


Table VIII-1. Physical Properties of 1,3,5-trinitrobenzene.*

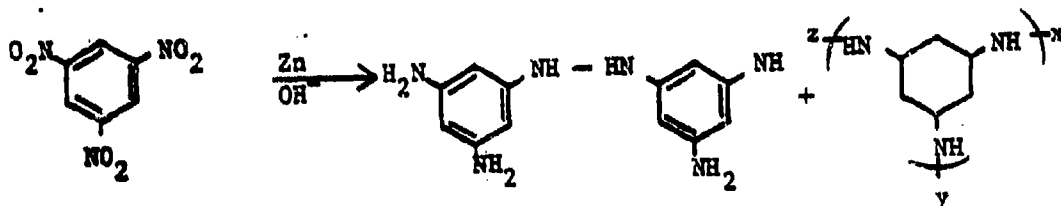
Physical Form @ 20°C:	dimorphous solid: Form I (most common) orthorhombic bipyramidal plates; Form II-plates
Color:	pale yellow
M.P.	122.5°C (Form I) 61°C (Form II)
B.P.	315°C @ 760 mm Hg 175°C @ 2 mm Hg sublimes with careful heating; explodes on rapid heating
Crystal Density:	d_4^{20} 1.76 d_4^{152} 1.4775
Solubility:	water - 0.0278 g/100 g @ 15°C 0.102 g/100 g @ 50°C 0.498 g/100 g @ 100°C acetone - 59.105 g/100 g @ 17°C 160.67 g/100 g @ 50°C methanol - 3.759 g/100 g @ 17°C 7.62 g/100 g @ 50°C 95% ethanol - 1.392 g/100 g @ 17°C 3.52 g/100 g @ 17°C ethyl ether - 1.703 g/100 g @ 17°C benzene - 6.176 g/100 g @ 17°C 25.70 g/100 g @ 50°C ethyl acetate - 29.826 g/100 g @ 17°C 52.40 g/100 g @ 50°C pyridine - 112.605 g/100 g @ 17°C 194.43 g/100 g @ 50°C

*References: Desvignes, 1931; Windholz, 1976; Sax, 1976; Hawley, 1977.

Reduction of mononitrobenzene with Zn in base, or with LiAlH_4 , produces N,N'-diphenyl hydrazine (March, 1968).

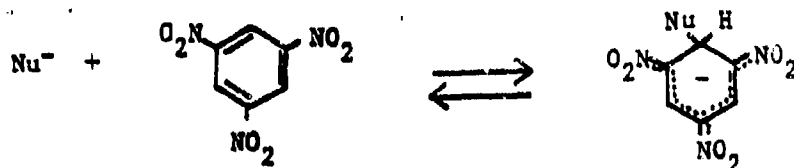


Reductive coupling of 1,3,5-TNB may give a polymeric product.

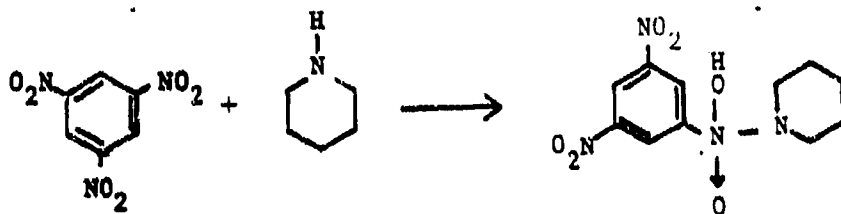


Electrophilic substitutions on a benzene ring are well known and considered the typical reaction of benzene derivatives. A nitro substituent on the ring decreases the reactivity towards electrophilic attack. The combined effects of three nitro groups makes trinitrobenzene particularly non-reactive toward electrophilic attack. The chemistry of trinitrobenzene is not typical benzene chemistry. The electron withdrawing effect of the nitro groups renders 1,3,5-TNB susceptible to nucleophilic rather than electrophilic attack.

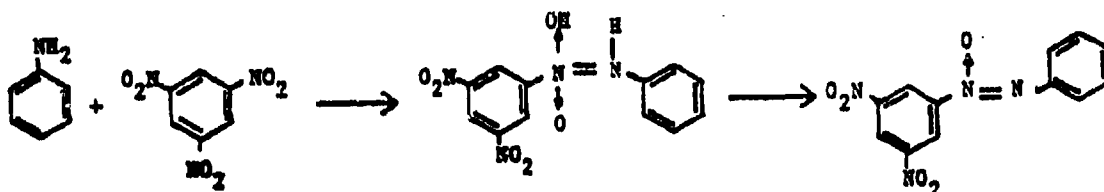
The predominant reaction of 1,3,5-TNB with a variety of nucleophiles is formation of a Meisenheimer complex (Bernasconi, 1970).



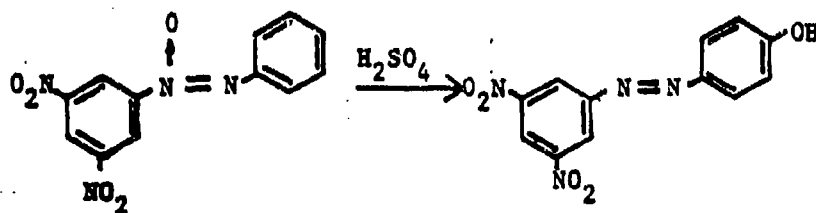
The reaction is well known with hydroxy, alkoxy and amine nucleophiles. Amines can undergo a second reaction with 1,3,5-TNB involving nucleophilic attack at a nitro group to form an oxyhydroxylamine.



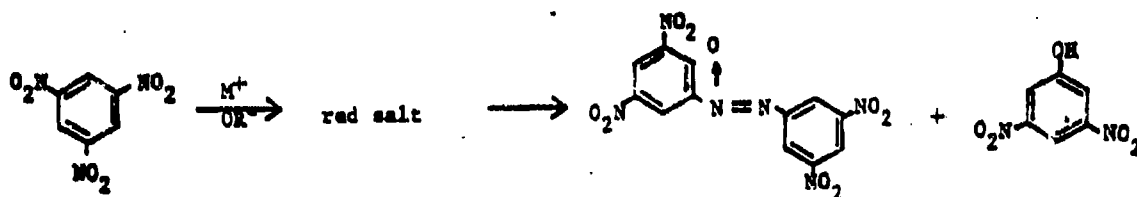
Oxyhydroxylamine formation is favored in water (Bernasconi, 1970). The adduct from a primary amine will eliminate water and form an azoxy compound.



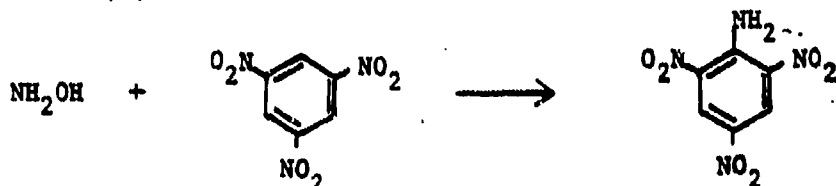
Azoxybenzenes in acid undergo a transformation known as the Wallach rearrangement.



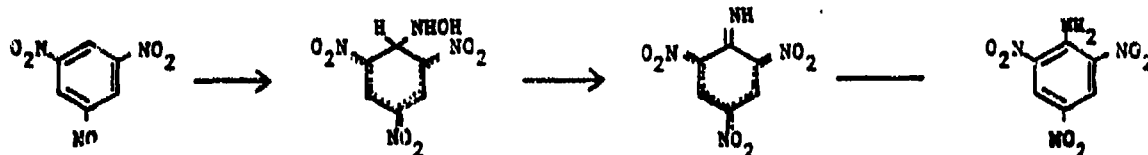
Treatment of 1,3,5-TNB with metal hydroxides in alcohol produces a red color due to salt formation. Continued alkaline treatment gives a bimolecular condensation product and 3,5-dinitrophenol.



Hydroxylamine in cold alcoholic solution reacts with 1,3,5-TNB to produce 2,4,6-trinitroaniline, known as picramide.



Presumably the Meisenheimer complex is formed first, followed by elimination of water and protonation.

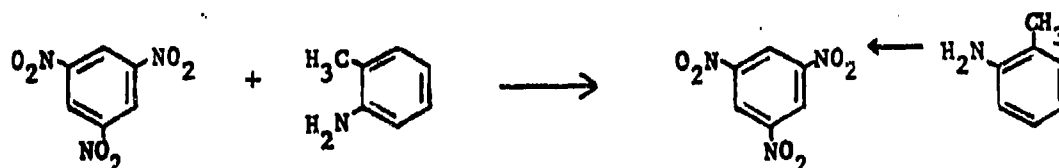


The thermal decomposition of 1,3,5-TNB vapors has been investigated (Maksimov and Egorycheva, 1971). The gaseous products were N_2 , CO, CO_2 , H_2O and small amounts of NO. No nitrogen dioxide was found.² A multi-component liquid residue product was formed. Possible constituents were benzene, phenol, aniline, biphenyl, and their nitro and nitroso derivatives. A brown film of nonuniform make-up formed on the vessel wall during decomposition. Spectroscopic investigation indicated the presence of unsaturated aromatic bonds and the presence of C- NO_2 functionality.

2. Sampling and Analysis

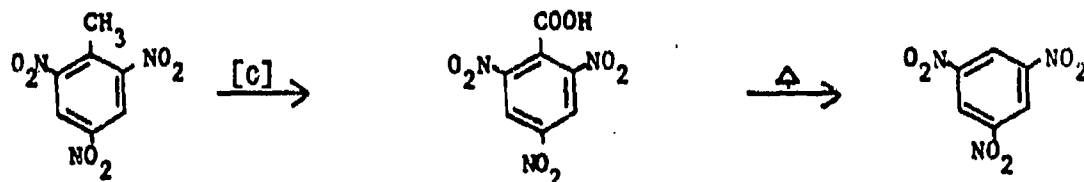
Analytical techniques for 1,3,5-TNB have been developed in conjunction with the analysis of explosive mixtures. Most of the procedures have been designed to enable analysis in the presence of chemically similar compounds.

Thin layer chromatography (TLC) of trinitrobenzenesamine charge transfer complexes has been used for the separation and identification of explosive components. 1,3,5-TNB reacts with an aromatic amine to form a colored charge transfer complex.



Qualitative identification of as little as 2 μg of material in the presence of trinitrotolulene (TNT), dinitrobenzene (DNB), and other aromatic nitro compounds is possible with this method (Parihar *et al.*, 1968).

Gas chromatographic (GC) methods have been developed for monitoring the composition of the organic phase of a continuous TNT production process (Dalton *et al.*, 1972). GC in tandem with high resolution mass spectrometry has also been used in analysis of TNT impurities (Chang, (1971). Quantitative estimation of TNB is hindered by the presence of trinitrobenzoic acid, an oxidation product of TNT. High injection port temperatures cause decarboxylation, raising the apparent TNB concentration.

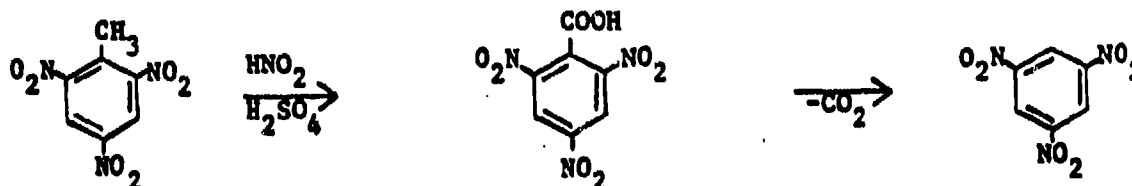


Infrared spectroscopy has been investigated for explosives analysis. It is a dated technique, useful primarily for identification of simple mixtures (Pristera *et al.*, 1960).

D. Uses of 1,3,5-trinitrobenzene in Army Munitions Production

1. Purposes

Although 1,3,5-TNB is an explosive, it is not currently used by the Army for this purpose. It is, however, a by-product in the manufacture of TNT. Under the conditions employed during the nitration of toluene, competitive oxidation of the methyl group to a carboxyl group can occur forming 2,4,6-trinitrobenzoic acid (2,4,6-TNBA). This acid is then decarboxylated to form 1,3,5-TNB.



Decarboxylation of 2,4,6-TNBA occurs mainly in the nitrators. However some decarboxylation is observed in the Sellite washers due to the high temperatures and alkaline conditions (Kohlbeck *et al.*, 1973). The direct nitration of benzene to 1,3,5-TNB is not kinetically favored. Therefore, the major route of any 1,3,5-TNB formation is through the carboxylic acid. Kohlbeck *et al.* (1973) have analyzed the nitrobody phase in each of the six nitrators in the continuous process. They found the following concentrations of 2,4,6-TNBA:

	<u>Nitrator No.</u>					
	1	2	3	4	5	6
Percent TNBA	0.43	0.92	0.78	0.76	0.45	0.18

The amount of 2,4,6-TNBA in the nitrobody phase increases to a maximum in the second nitrator then decreases to 0.18% in the sixth nitrator. This decrease is probably due to decarboxylation to 1,3,5-TNB. Any residual 2,4,6-TNBA is removed in the Sellite washer. However, the 1,3,5-TNB is not removed beyond its solubility in the purification process and ends up in the final product. Analysis of the TNT product exudates from the continuous and batch process show a higher 1,3,5-TNB content resulting from the continuous process (Kohlbeck *et al.*, 1973):

- RAAP (continuous)	0.59 - 0.70%	1,3,5-TNB
- VAAP (batch)	0.14 - 0.20%	1,3,5-TNB
- JAAP (batch)	0.16%	1,3,5-TNB

2. Estimated or Speculated Losses of 1,3,5-TNB from TNT Manufacture

a. Process Losses

Chromatographic studies (Kohlbeck *et al.*, 1973) indicate that 1,3,5-TNB is more volatile than TNT. Thus 1,3,5-TNB would be expected to

end up in the batch scrubber effluents in a slightly higher relative proportion than it is in the TNT. Losses of 1,3,5-TNB to the acids wash (yellow) water and the Sellite washer (red) water would also be expected due to the greater water solubility of 1,3,5-TNB (0.04g/100g) compared to that of TNT (0.02g/100g).

The red and yellow water are not discharged into the environment. The yellow water is returned to the second nitrator. Excess yellow water is combined with the red water (Patterson *et al.*, 1976). The red water is concentrated in rotary kilns to about 35-40% solids (TRW, 1973). The concentrated liquid is either sold to the paper industry or incinerated to a dry residue. The dry residue is then disposed of in landfills or stockpiled. Thus, the possibility of ground and surface water contaminant from this waste exists.

The evaporator condensate from the red water condensation process contains ~ 15 mg/l nitrobenzenes (Patterson *et al.*, 1976). Since 1,3,5-TNB is more volatile than TNT, a relatively high proportion of 1,3,5-TNB could end up in this condensate. Currently this condensate is discharged untreated at all plants (Patterson *et al.*, 1976).

Since 1,3,5-TNB concentrations are not routinely monitored, it is difficult to estimate the amount of 1,3,5-TNB which might be entering the environment from TNT manufacturing facilities. A sample of RAAP condensate wastewater was analyzed for 1,3,5-TNB by Epstein *et al.* (1975). They found about 0.6% of the nitrogen containing organics were 1,3,5-TNB and 8% TNT or a TNT/1,3,5-TNB ratio of 145/1. Applying this ratio to the data in Table I-7 (Section I of this report), a 1,3,5-TNB concentration in the effluent can be calculated. With these assumptions, RAAP discharges of 1,3,5-TNB would be expected to be 0.39 lb/line/day or 0.77 lb/day with two continuous lines operating.

Analysis of 79 condensate water samples from VAAP (1 continuous line in operation) indicates only occasional detectable concentrations of 1,3,5-TNB (Barkley, 1978). Of the 79 samples, 76 contained no detectable 1,3,5-TNB. A maximum of 0.2 mg/l was found in the remaining samples. VAAP has the capability of operating 6 CIL continuous and 6 batch lines. Approximately 0.39 lb/day from each continuous line and 0.07 lb/day from each batch line or 2.76 lb/day could be discharged from VAAP at full capacity. Likewise, discharges from JAAP at full capacity would be 2.55 lb/day (6 CIL continuous and 3 batch lines).

b. 1,3,5-TNB Production in the Environment

In addition to the 1,3,5-TNB in the process effluent, photolysis of TNT has also been shown to be a source of 1,3,5-TNB in the environment. Burlinson *et al.* (1973) have shown the occurrence of ~1% photoconversion of TNT to 1,3,5-TNB by sunlight. Thus photoconversion could add an additional 1.10 lb/day (2 lines operating) of 1,3,5-TNB to RAAP wastes. At full capacity, photochemical conversion could add another 3.94 lb/day and 3.64 lb/day of 1,3,5-TNB to VAAP and JAAP wastes.

c. Estimated 1,3,5-TNB Discharges from TNT Manufacture

Combining the 1,3,5-TNB from the process and photochemical sources, discharge rates and river concentrations at full production can be calculated for RAAP, JAAP, and VAAP. These data are presented in Table VIII-2. For these calculations, JAAP discharges were assumed to be similar to those from RAAP. Newport incinerates all their nitrobody containing wastes.

Table VIII-2. Estimated Discharges and River Concentrations of 1,3,5-TNB at Full TNT Production.

<u>Plant</u>	<u>No. of Lines</u>	<u>Total Discharge Rates lb/day</u>	<u>River</u>	<u>River Flow mgd</u>	<u>River Concentration ppb</u>
RAAP	2 continuous	1.9	New	2,380	0.1
VAAP	6 batch 6 continuous	6.7	Tennessee	23,750	0.03
JAAP	6 continuous 6 batch	6.2	Illinois	5,390	0.14

3. Estimated or Speculated Losses of 1,3,5-TNB from TNT Blending Operations

TNT is blended with RDX or HMX at HAAP. The blending operation (incorporation) was described in Section I.A.1.f, page 40 of this report. As discussed earlier 0.1 to 0.7% of the final TNT product is 1,3,5-TNB. At full production, 110 mil/lb of TNT would be used at HAAP each year. Of this TNT, 110,000 to 770,000 lb is 1,3,5-TNB. Estimated discharges of TNT at full production run as high as 650 lb/day. If a comparable percentage of 1,3,5-TNB were lost, the discharge would be 0.65 to 4.6 lb/day. However, 1,3,5-TNB is approximately twice as soluble as TNT. Therefore as much as 1.3 to 9.1 lb of 1,3,5-TNB could be discharge per day from HAAP. Photolysis of TNT could lead to an additional 6.5 lb/day of 1,3,5-TNB in the Holston River. The resulting Holston River concentration (assuming full mixing) could be as high as 0.9 ppb. However, local river concentrations could reach ten times this concentration.

4. Estimated or Speculated Losses of 1,3,5-TNB from LAP Operations

Cornhusker, Kansas, Lone Star and Louisiana AAP's dispose of generated pink water from LAP operations by evaporation in ponds or basins. Samples of the wastewaters in sumps at Louisiana AAP had TNT and 1,3,5-TNB concentrations of 213 and 2 mg/l, respectively (Burlinson and Glover, 1976). Samples from the leaching pond were also analyzed in this study. This pond contained 20 mg/l TNT and 18 mg/l 1,3,5-TNB. These data indicate the formation of 1,3,5-TNB from photolysis of TNT. There is no information on the

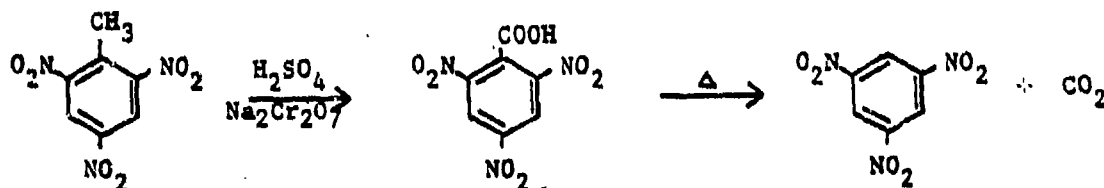
leaching of 1,3,5-TNB into the ground water.

Iowa and Joliet AAP use carbon adsorption to treat their pink water effluents. There is very little information concerning the influent to and effluent from these columns. Burlinson and Glover (1976) analyzed the effluent from the carbon columns at Iowa AAP. They did not detect any 1,3,5-TNB in this effluent.

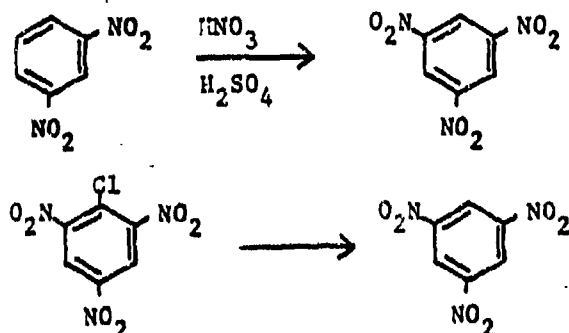
E. Uses of 1,3,5-trinitrobenzene in Civilian Community

1. Production Methodology

The most economical preparation method for 1,3,5-TNB is from trinitrotoluene. Oxidation of trinitrotoluene with H_2SO_4 and sodium dichromate is followed by decarboxylation in boiling water. CO_2 is liberated and 1,3,5-TNB precipitates.



Trinitrobenzene may also be produced by direct nitration of m-dinitrobenzene or reduction of picryl chloride.



2. Manufacturers, Production, and Capacities

There are currently no major U.S. manufacturers of 1,3,5-TNB. Both Eastman Organic and J. T. Baker Chemicals formerly supplied it. Aldrich Chemical lists 1,3,5-TNB in their catalog of available chemicals but does not maintain any in stock.

3. Usages

There are no major non-explosive uses of 1,3,5-TNB.

4. Future Trends

There are no anticipated future uses of 1,3,5-TNB. It is chemically unsuitable as a synthetic intermediate. Due to the dangers of handling 1,3,5-TNB, it is an industrially undesirable chemical.

5. Documented or Speculated Occurrences in the Environment

Occurrences of 1,3,5-TNB in the civilian environment have not been reported.

F. Comparison of Army and Civilian Uses of 1,3,5-TNB

1,3,5-TNB is only used in research quantities in the civilian community. It is also not used in the military sector. However, 1,3,5-TNB is present to the extent of 0.1 to 0.7% of the TNT final product. It is also present in the aqueous effluents from the military manufacturing blending and LAP of TNT. No civilian facilities are currently producing TNT. DuPont and Mobay manufacture DNT. Some 1,3,5-TNB might be found in their waste water or product. However, this discharge, if any, would be small compared to the military pollution from 1,3,5-TNB. Thus, 1,3,5-TNB environmental discharge is a unique military problem.

G. Toxicological and Environmental Hazards of 1,3,5-trinitrobenzene

1. Mammalian Toxicity

The acute and chronic effects of 1,3,5-TNB on mammals are presented in Table VIII-3. The LD50 for 1,3,5-TNB is over 500 mg/kg for rodents. Gorski (1969) did not find 1,3,5-TNB carcinogenic to BALB/C mice. However, he did observe that 1,3,5-TNB increases the carcinogenic activity of 3-methylcholanthrene in mice. Buckell and Richardson (1950) listed 1,3,5-TNB as a substance which produced Heinz bodies in erythrocytes. These bodies indicate the development of anemia. Bredow and Junz (1943) show that both 1,3-DNB and 1,3,5-TNB can cause the formation of methemoglobin. Methemoglobin is formed from oxyhemoglobin and results in the lack of oxygen availability to the cells. Although 1,3,5-TNB methemoglobin levels are not as high as 1,3-DNB, 1,3,5-TNB formation is faster (1 hour to 10 hours).

The available data indicate that 1,3,5-TNB is very toxic when administered in subacute and chronic doses. Bioaccumulation of this compound in mammalian tissues has not been studied, nor have any human toxicological responses been reported. No studies were found in the literature dealing with the mutagenic or teratogenic effects of 1,3,5-TNB.

Human exposure to 1,3,5-TNB is mainly limited to handling of TNT. Some of the toxic effects of 1,3,5-TNB could be overlooked in this handling due to the greater exposure to TNT.

Table VIII-3. Acute and Chronic Animal Toxicity of 1,3,5-trinitrobenzene.

Species	Dose (mg/kg)	Route of Adminis.	Period of Exposure	Effects	Reference
Dogs	100	Oral	Daily for 4 days	Female dog developed convulsions, anorexia, soft feces, alterations of erythrocyte morphology, 11.4% methemoglobin; male dog developed 21.8% methemoglobin; treatment was discontinued due to poor health of dogs	Fogleman <i>et al.</i> , 1953
Dogs	25	Oral	17 doses over 54 days	Female dog developed anoxia, depression, and emesis during the first 10 days but recovered thereafter; male developed generalized muscular stiffness with ataxia after 14 days which persisted to end of study; maximum methemoglobin levels of 23.4% in the female and 11.8% in the male; spleen and liver were enlarged and signs of kidney degeneration were present in both male and female	Fogleman <i>et al.</i> , 1955
Mice	572	Oral	Once	LD50	Timofievskaya and Rodinova, 1973
Rat	505	Oral	Once	LD50	Fogleman <i>et al.</i> , 1955

2. Aquatic Toxicity

Several studies have been conducted to determine the distribution of 1,3,5-TNB in receiving waters from TNT manufacture, blending and LAP operations (Huff *et al.*, 1975a,b,c,d; Jerger *et al.*, 1976). In general 1,3,5-TNB was below the detection limit in both the water and sediment samples (0.2 mg/l for water and 20 mg/l for sediment). However, studies conducted at VAAP, showed increasing 1,3,5-TNB down river from the discharge points. Concentrations up to 66.3 mg/l were detected in water samples taken from points along Waconda Bay (Sullivan *et al.*, 1977). Sediments contained up to 304 mg/l of 1,3,5-TNB. Thus, it appears that the major source of 1,3,5-TNB pollution is from photoconversion of TNT.

As indicated in Table VIII-4, 1,3,5-TNB is toxic to aquatic organisms.

Table VIII-4. Effect of 1,3,5-trinitrobenzene on Aquatic Organisms.

<u>Species</u>	<u>Conc.</u> <u>mg/l</u>	<u>Water</u>	<u>Temp.</u> <u>°C</u>	<u>Effect</u>	<u>Reference</u>
Fathead minnow (<i>Pimephales promelas</i>)	1.03	soft	20	96-hr LC50	Liu & Bailey, 1977
Water flea (<i>Daphnia magna</i>)	27.0	soft	20	48-hr LC50	"

At 10 mg/l fish (*Kuhlia sandvicensis*) showed violent irritant activity (Hiatt *et al.*, 1953). Irritant activity was observed with concentration of 1,3,5-TNB as low as 0.1 mg/l. Huff *et al.* (1975c) found 1,3,5-TNB present in fish tissues (river carpsucker and longear sunfish), but they could not quantify the levels, due to broadening of the gas chromatographic peaks. Liu and Bailey (1977) found aquatic organisms bioaccumulate TNT to the extent of 200-400 times the amount found in the water. A similar bioaccumulation factor would be expected for 1,3,5-TNB. Thus, 1,3,5-TNB could be biomagnified in the food chain. The degree of 1,3,5-TNB bioaccumulation and its entry into the food chain require further investigation.

3. Microorganism Toxicity

As shown in Table VIII-5 the growth of microorganisms can be inhibited by 1,3,5-TNB. The most sensitive organisms was *Streptococcus* sp. which was inhibited by 1 mg/l of 1,3,5-TNB. With a mixture of microorganisms, predominantly *Pseudomonas* sp., Chambers *et al.* (1963) found a

Table VIII-5. Growth Inhibition of Bacteria and Fungi by 1,3,5-TNB.

Species	Conc. mg/l	Medium	Effect	Reference
Bacteria				
<i>Streptococcus</i> sp.	1	--	inhibition	Lecoq & Landrin (1951)
Human tuberculin bacillus	2	--	"	"
<i>Staphylococcus aureus pyogenes</i>	21	--	Inhibition threshold	Zsolnai (1970)
<i>Staphylococcus albus</i>	8.5	--	"	"
<i>Escherichia coli communis</i>	8.5	--	"	"
<i>Aerobacter aerogenes</i>	21	--	"	"
<i>Proteus vulgaris</i>	8.5	--	"	"
<i>Staphylococcus oxford</i>	35	--	complete inhibition	Secareanu <i>et al.</i> (1966)
<i>Escherichia coli</i>	35	--	"	"
<i>Klebsiella pneumoniae</i>	100	--	"	"
Fungi				
<i>Trichoderma viride</i>	21	agar	50% inhibition	Simon & Blackman (1953)
<i>Trichophyton gypseum</i>	43	--	inhibition threshold	Zsolnai (1970)
<i>Epidermophyton</i>	43	--	"	"

relatively low oxygen uptake by the organisms and little oxidation of the 1,3,5-TNB. Bringman and Kuhn (1971) used a two stage process, the first stage contained *Azobacter agilis* and the second stage activated sludge. After 36 hours 95-97% of the 1,3,5-TNB was reduced. Villanueva (1961) found that a strain *Noocardia V.* could metabolize 1,3,5-TNB to an arylamine.

From this data it seems that 1,3,5-TNB is fairly persistent in the environment. However, if released at a constant rate, organisms could be present to metabolize the compound.

4. Phytotoxicity

The phytotoxicity of various nitrosubstituted benzenes was studied by Simon and Blackman (1953). The toxic properties of these chemicals were determined by the concentrations required to reduce the growth rate of *Trichoderma viride* to one-half. These data are presented in Table VIII-6.

Table VIII-6. Concentration of Nitrobenzenes Required for 50% Inhibition of Growth Rate of *Trichoderma viride*.

<u>Component</u>	<u>Concentration, mg/l</u>
Nitrobenzene	689
o-dinitrobenzene	50
p-dinitrobenzene	20
1,3,5-trinitrobenzene	21

Their data indicate greater phytotoxicity for ortho and para substituted nitro groups. However, these data indicate 1,3,5-TNB to be phytotoxic in the low ppm range.

5. Environmental Fate

Newell *et al.* (1976) have shown that 1,3,5-TNB is not lost from the environment by photolysis. Some losses from the aquatic environment would be expected due to volatility (Barkley, 1978). Microorganism degradation also occurs to some extent. Another possible loss of 1,3,5-TNB from the aquatic environment is due to chemical reactions. Complex formation or derivatization would reduce the 1,3,5-TNB concentration. If these reactions occur, volatilization and microorganism degradation will be slower than for free 1,3,5-TNB.

Although the data is sketchy, it appears that 1,3,5-TNB concentrates in the sediment and bioaccumulates in aquatic organisms. The effect of these concentration factors are unknown at this time. Further studies

on bioaccumulation effects on the food chain, sediment accumulation and microbial degradation and resultant products under naturally occurring conditions require further investigation.

6. Availability of Literature for Phase II

There is sufficient data on the toxicological hazards of 1,3,5-TNB. The environmental data is sketchy; however, an evaluation of foreign literature and a detailed comparison with nitrobenzenes and TNT would be useful.

H. Regulations and Standards

Since 1,3,5-TNB is not an industrially produced or used chemical, there are no regulations which are specific to its discharge, handling or transport. It is, however, listed in EPA Toxic Substances Control Act Candidate List of Chemical Substances (1977).

I. Conclusions and Recommendations

The data obtained and evaluated during this problem definition study on 1,3,5-trinitrobenzene indicate the following conclusions.

1. 1,3,5-TNB is a military unique compound; it is not manufactured or used by the Civilian community.
2. 1,3,5-TNB is a by product of TNT manufacture which ends up in the final product at a concentration of 0.1 to 0.7%.
3. 1,3,5-TNB enters the environment from the manufacture, blending and loading of TNT.
4. It is produced in the environment by photodecomposition of TNT.
5. 1,3,5-TNB is highly toxic to aquatic life and mammals.
6. Degradation occurs very slowly in the environment with accumulation in sediments and bioaccumulation in fish observed.

Due to its toxicity and military uniqueness, 1,3,5-trinitrobenzene is recommended for a detailed Phase II toxicological and environmental evaluation. The following studies are also recommended in order to clarify the environmental and treatment problems due to the chemical.

1. Additional sediment and fish analysis for 1,3,5-TNB be conducted at TNT manufacturing facilities when they again become operational and at Holston AAP.
2. A study be conducted on the ability of proposed treatment processes to remove 1,3,5-TNB from the effluent streams.

The questions which need to be answered are:

Will the proposed biotreatment facilities at HAAP degrade 1,3,5-TNB to a more toxic nitroso or amino compound as has been found with biodegradation of TNT?

Will the presence of 1,3,5-TNB change the bed to volume breakthrough on the carbon adsorption columns and will it be efficiently removed from the effluent?

J. References

- Barkley Jr., J.J. (1978), "Condensate Water Compounds," Memorandum to J. Gareth Pearson.
- Bernasconi, C.F. (1970), "Intermediates in Nucleophilic Aromatic Substitution," *J. Amer. Chem. Soc.*, 92.
- Bredow, M. and Jung, F. (1943), "Studien Ueber Methämoglobinbildung," *Aroh. Exp. Path. Pharmacol.*, 200, 335, in Howard *et al.* (1976), "Investigation of Selected Potential Environmental Contaminants: Nitroaromatics," EPA Contract No. 68-01-2999.
- Bringmann, G. and Kuehn, R. (1971), "Biological Decomposition of Nitrotoluenes and Nitrobenzenes by *Acetobacter Agilis*," *Gesundh.-Ing.*, 92(9), 273.
- Buckell, M. and Richardson, J. (1950), "The Significance of Heinz Bodies in the Erythrocyte," *Brit. J. Ind. Med.*, 7, 131.
- Burlinson, N.E. and Glover, D.J. (1976), "Photochemistry of TNT and Related Nitrocompounds - Investigation of the Pink Water Problem," Quarterly Progress Report No. 8, MESA 6768.
- Burlinson, N.E.; Kaplan, L.A. and Adams, C.E. (1973), "Photochemistry of TNT: Investigation of the 'Pink Water' Problem," NOLTR 73-172, Naval Ordnance Laboratory, MD.
- CRC (1974), *Spectral Data and Physical Properties of Chemical Compounds*, 2nd ed., Chemical Rubber Co., Cleveland, Ohio, 1-VII.
- Chambers, C.; Tabak, H.H. and Kahler, P.W. (1963), "Degradation of Aromatic Compounds by Phenol-adapted Bacteria," *J. Water Poll. Control Fed.*, 35(12), 1517.
- Chang, T.L. (1971), "Identification of Impurities in Crude TNT by Tandem GC-MS Technique," *Anal. Chim. Acta.*, 53, 445.
- Dalton, R.W.; Kohlbeck, J.A. and Bollater, W.T. (1970), "Gas Chromatographic Analysis of Trinitrotoluene from the Continuous Process," *J. Chromatogr.*, 50, 219.
- Desvergues, L. (1931), "1,3,5-trinitrobenzene or Benzite," *Chim. Ind.*, 25 (3-17), 291.
- EPA (1977), Toxic Substances Control Act Candidate List of Chemical Substances, PL 94-469.
- Epstein, J.; Sommer, H.Z. and Hackley Jr., B.E. (1975), "Environmental Quality Standards Research on Wastewaters of Army Ammunition Plants," Final Comprehensive Report on Project MRDC (SGO).
- Fogleman, R.W.; Elsea, J.R.; Paynter, O.E. and Kundzins, W. (1955), "Toxicity of Trinitrobenzene - Aniline Complex, A Rodent Repellent," *Agric. Food Chem.*, 3(11), 936, in Howard *et al.* (1976), "Investigation of

Selected Potential Environmental Contaminants: Nitroaromatics,"
EPA Contract No. 68-01-2999.

- Gorski, T. (1969), "Biological Role of Charge Transfer Complexes of Aromatic Hydrocarbon oxy-derivatives in Chemical Carcinogenesis," *Neoplasma*, 16(4), 403, in Chem. Abstr. 72:1656s.
- Hawley, G.G. (1977), *The Condensed Chemical Dictionary*, 9th edition, Van Nostrand Reinhold Co., NY.
- Hiatt, R.; Naughton, J. and Matthews, D. (1953), "Relation of Chemical Structure to Irritant Responses in Marine Fish," *Nature*, 172(4385), 904.
- Huff, B.L.; Duckert, W.D.; Barding, P.G.; Wheeler, J.H.; Hogan, T.M. and Bogardus, R.B. (1975a), "Aquatic Field Surveys at Radford, Holston, Volunteer, and Milan Army Ammunition Plants-I. Radford," AMRDC, DAMD-17-74-C-4138.
- Huff, B.L.; Duckert, W.D.; Barding, P.G.; Wheeler, J.H. and Bogardus, R.B. (1975b), "Aquatic Field Surveys at Radford, Holston, Volunteer and Milan Army Ammunition Plants-II. Holston," AMRDC DAMD-17-74-C-4138.
- Huff, B.L.; Duckert, W.D.; Barding, P.G.; Wheeler, J.H.; Hogan, T.M. and Bogardus, R.B. (1975c), "Aquatic Field Surveys at Radford, Holston, Volunteer and Milan Army Ammunition Plants-III. Volunteer," AMRDC DAMD-17-74-C-4138.
- Huff, B.L.; Duckert, W.D.; Barding, P.G.; Wheeler, J.H.; Hogan, T.M. and Bogardus, R.B. (1975d), "Aquatic Field Surveys at Radford, Holston, Volunteer and Milan Army Ammunition Plants-IV. Milan," AMRDC DAMD-17-74-C-4138.
- Jarger, D.E.; Simon, P.B.; Weitzel, R.L. and Schenk, J.E. (1976), "Aquatic Field Surveys at Iowa, Radford and Joliet Army Ammunition Plants, Microbiological Investigations, Iowa and Joliet Army Ammunitions Plants," AMRDC.
- Kohlbeck, J.A. and Chandler Jr., C.D. (1973), "Continuous TNT Characterization Study (PE-238); Continuous TNT Process Control and Characterization Study - Extension (PE-289)," in Howard *et al.* (1976), "Investigation of Selected Potential Environmental Contaminants: Nitroaromatics," EPA Contract No. 68-01-2999.
- Lecoq, R. and Landrin, P. (1951), "Importance of the Position and Mobility of Nitro Groups on the Antibiotic Action of Benzene Derivatives," *Compt. rend.*, 232, 762, in Chem. Abstr (1952), 6701.
- Liu, D. and Bailey, H.R. (1977), "Toxicity of TNT Wastewater to Aquatic Organisms," Monthly Progress Report No. 27.

- Maksimov, Y.Y. and Egorycheva, G.I. (1971), "Composition of Products of the Thermal Decomposition of Trinitrobenzene Vapors," *Kinet. Katal.*, 12, 821.
- March, J. (1968), *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, McGraw-Hill Book Co., New York.
- Newell, G.W., Dilley, J.V. and Spangford, R.J. (1976), "Mammalian Toxicological Evaluations of TNT Wastewater ("Pink Waters")," AMRDC Contract No. DAMD17-76-C-6050.
- Parihar, D.B.; Sharma, S.P. and Verma, K.K. (1968), "Trace Analysis of Explosives as Pi Complexes," *J. Forensic Sci.*, 13, 246.
- Patterson, J.; Shapira, N.I.; Brown, J.; Duckart, W. and Polson, J. (1976), "State-of-the-Art: Military Explosives and Propellants Production Industry III Wastewater Treatment," Industrial Environmental Research Laboratory - Cinn.
- Priester, F.; Halik, M.; Castelli, A. and Fredericks, W. (1960), "Analysis of Explosives Using Infrared Spectroscopy," *Anal. Chem.*, 32, 495, in Howard *et al.* (1976), "Investigation of Selected Potential Environmental Contaminants: Nitroaromatics," EPA Contract No. 68-01-2999.
- Sax, N.I. ed. (1976), *Dangerous Properties of Industrial Materials*, 2nd ed., Reinhold Publ. Corp., NY., 1292.
- Secareanu, S.; Maier, N. and Vaida, T. (1966), "Bacteriostatic Action of 2,4,6-trinitrobenzaldehyde and 1,3,5-trinitrobenzene on some micro-organisms," *Z. Med. Mikrobiol. Immunol.*, 153(1), 13.
- Simon, E.W. and Blackman, G.E. (1953), "The Effects of the Degree of Nitration on the Toxicity of Phenol and Other Substitution Benzenes," *J. Exp. Bot.*, 4(11), 235.
- Sullivan, J.H.; Putnam, H.D., Kairn, M.A.; Swift, D.R. and Pruitt, B.C., Jr. (1977), "Winter Field Surveys at Volunteer Army Ammunition Plant, Chattanooga, Tennessee, Final Report, Water and Air Research, Inc.
- Timofievskaya, L.A. and Rodinova, R.P. (1973), "Comparative Evaluation of the Toxicity of Some Aromatic Compounds," *Tokoiol. Nov. Prom. Khim. Veshchestu*, 13, 138, in Chem. Abstr. 80:10940X.
- TRW (1973), "Army Munitions Plants Modernization Program - Pollution Abatement Review - Final Report," Report No. 96020.007.
- Villanueva, J.R. (1961), "Organic Nitro Compounds Reduced by *Nocardia V.*," *Microbiol. Espan.*, 14, 157.
- Windholz, M. (1976), *The Merck Index*, 9th edition, Merck and Co., Inc., Rahway, N. J.

Zsolnai, T. (1970), "Die Antimikrobielle Wirkung von Potentiellen Thio-reagen-
tien," *Zbl Bakt I Abt Orig.*, 214, 507.

ABBREVIATIONS AND SYMBOLS

Å	- Angstroms, 10^{-8} meter
AAP	- Army Ammunition Plant
atm	- atmosphere
Bldg	- building
BOD	- biological oxygen demand
B.P.	- boiling point
BSX	- intermediate in RDX manufacture - $\text{CH}_3\text{COOH}_2\text{N}(\text{NO}_2)-(\text{CH}_2)_2-\text{N}-\text{NO}_2$
°C	- degree Centigrade
CA	- Chemical Abstracts
CAAP	- Cornhusker Army Ammunition Plant
cal	- calorie
CAS	- Chemical Abstracts Service
cc	- cubic centimeter
CH_2O	- formaldehyde
8CI	- 8th cumulative index
9CI	- 9th cumulative index
CIL	- Canadian Industries Limited
cm^{-1}	- wavenumber
CO	- carbon monoxide
CO_2	- carbon dioxide
COD	- chemical oxygen demand
d	- density
Δ	- heat
DMA	- dimethylamine
1,3-DNB	- 1,3-dinitrobenzene
DNBA	- dinitrobenzoic acid
DNT	- dinitrotoluene
E+	- electrophile
ε	- molar absorptivity coefficient
EC50	- concentration which exhibits an effect on 50% of the exposed population
EDTA	- ethylene diamine tetracetic acid
F	- female

ABBREVIATIONS AND SYMBOLS (continued)

ft	- foot
FW	- filtered water
g	- gram
GC	- gas chromatography
gpd	- gallons per day
gpm	- gallons per minute
H ₂	- hydrogen
ΔH _p	- heat of combustion
HAAP	- Holston Army Ammunition Plant
HDC	- Holston Defense Corporation
HMPA	- hexamethylphosphoramide
HMX	- octahydro-1,3,5,7-tetranitro-s-tetrazine
HNO ₃	- nitric acid
H ₂ O	- water
hrs	- hours
H ₂ SO ₄	- sulfuric acid
hu	- high energy
IAAP	- Iowa Army Ammunition Plant
IC	- inorganic carbon
in	- inch
I.P.	- intraperitoneal
I.R.	- infrared
I.V.	- intravenous
JAAP	-Joliet Army Ammunition Plant
k	- rate constant
KAAP	-Kansas Army Ammunition Plant
K _b	- basicity constant
Kcal	- kilocalorie
kg	- kilogram
L	- liter
λ	- wavelength of light
LA	- Los Angeles

ABBREVIATIONS AND SYMBOLS (continued)

LAAP	- Louisiana Army Ammunition Plant
LAP	- load, assembly and pack
lb	- pound
LD50	- dose necessary to kill 50% of the exposed population
LDLo	- lowest lethal dose
LSAAP	- Lone Star Army Ammunition Plant
M	- molar
MAAP	- Milan Army Ammunition Plant
MAC	- maximum allowable concentration
uc	- micro curries
ug	- microgram
mg	- milligrams
MGD	- million gallons per day
mil	- million
min	- minute
mu	- millimicron
mm	- millimeter
mM	- millimoles
mmol	- millimoles
MNA	- monomethylamine
MP	- melting point
n_D	- index of refraction
NAAP	- Newport Army Ammunition Plant
NAD	- nicotinamide adenine dinucleotide
NADH	- reduced nicotinamide adenine dinucleotide
NaOH	- sodium hydroxide
NDMA	- N-nitrosodimethylamine
ng	- nanogram
NH ₃	- ammonia
NH ₃ /N	- ammoniacal nitrogen
nm	- nanometer
NMR	- nuclear magnetic resonance
n.s.	- not specified

ABBREVIATIONS AND SYMBOLS (continued)

Nu	- nucleophile
O	- oxygen
O ₂	- oxygen
oc	- organic carbon
OH	- hydroxide
OSHA	- Occupational Safety and Health Administration
PBX	- plastic bonded explosives
PBNK	- plastic bonded explosive containing nylon or a vinylidene difluoride-hexafluoropropylene copolymer
X	- percent
pH	- log hydrogen ion concentration
ppb	- parts per billion
ppm	- parts per million
psi	- pounds per square inch
redn	- reduction
RDX	- hexahydro-1,3,5-trinitro-s-triazine
RO ⁻	- alkoxide ion
RW	- river water
s.c.	- subcutaneous
s.d.	- standard deviation
SEX	- octahydro-1-acetyl-3,5,7-trinitro-s-tetrazine
stm	- steam
SO ₂	- sulfur dioxide
T	- temperature
TAX	- hexahydro-1,3,5-dinitro-5-acetyl-s-triazine
TLC	- thin layer chromatograph
TLV	- threshold limit value
TMA	- trimethylamine
TMA-O	- trimethylamine oxide
1,3,5-TNB	- 1,3,5-trinitrobenzene
TNT	- trinitrotoluene
USSR	- United Soviet Socialist Republic

ABBREVIATIONS AND SYMBOLS (continued)

v - volume
VAAP - Volunteer Army Ammunition Plant
w - weight

DOCUMENT DISTRIBUTION LIST

25 copies

Commander
US Army Medical Bioengineering
Research and Development Laboratory
ATTN: SGRD-UEG
Fort Detrick, Frederick, MD 21701

4 copies

HQDA (SGRD-AJ)
Fort Detrick
Frederick, MD 21701

12 copies

Defense Documentation Center (DDC)
ATTN: DDC-TCS
Cameron Station
Alexandria, Virginia 22314

1 copy

Dean
School of Medicine
Uniformed Services University of
the Health Sciences
4301 Jones Bridge Road
Bethesda, Maryland 20014

1 copy

Superintendent
Academy of Health Sciences, US Army
ATTN: AHS-COM
Fort Sam Houston, Texas 78234